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FINAL REPORT
NO. M-56-1-ONR
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FC

Improved Liquid Propellants

HYDRAZINE DERIVATIVES

Metalectro

CORPORATION

LAUREL, MARYLAND

MAY 2 4 1956

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H Y D R A Z I N E

D E R I V A T I V E S

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CONTRACT FULFILLMENT

This report is submitted as the final report
in fulfillment of Contract Nonr-163(01) and
covers investigations performed during the
period September 1, 1950 to October 31, 1955.

ABSTRACT

All previous investigative work conducted under
Contract Nonr 163(01) is summarized in this
final report. A small amount of work which was
not described in any previous report is also in-
cluded. This new work includes the isolation
and characterization of trimethylene hydrazine,
monopropargyl hydrazine and N-methyl-N-propargyl
hydrazine. Further efforts to develop syntheses
for ethylenehydrazine and N-isocyanides are also
described.

I.   OBJECTIVES

From the inception of its work on Contract Nonr 163(01),
Metalectro Corporation has based its investigative program
on three general objectives.

Objective A:

To impart to conventional liquid rocket propellants su-
perior fuel characteristics through the addition of hydra-
zine.

Objective B:

To lower the freezing point of hydrazine below -40°C with-
out appreciably diminishing its theoretical performance by
incorporating additives into hydrazine.

Objective C:

To develop a homogenous liquid rocket propellant possess-
ing, in addition to the desirable properties of hydrazine,
a freezing point below -40°C, and increased stability at
elevated temperatures through the judicious substitution of
one or more of the hydrogen atoms of hydrazine with suitable
carbon-hydrogen radicals.

II.   GENERAL INTRODUCTION

With this final report the work on contract Nonr-163(01) is
brought to a close. The work under this contract was started
in September 1950, and during the intervening time there
have been shifts in views and changes of emphasis with re-
spect to rocket propellant requirements. In 1950 hydrazine
loomed as one of the most likely medium-energy fuels to be
generally employed for rocket propulsion. Although certain
deficiencies of hydrazine, particularly its high freezing
point, were apparent, it was assumed that a satisfactory
solution to these difficulties could be achieved ultimately.
At that time also there were still hopes to develop smooth
and efficient combustion of hydrocarbon fuels, such as JP-4,
with nitric acid, using no additives or hypergolic agents.
However, considerable interest had already been developed
in the use of hypergolic starting materials and hypergolic
fuels, and one of the problems which was receiving consider-
able attention was the search for a hypergolic fuel which
would be low in cost and which would give small ignition
delays even at low temperatures. In connection with the

latter investigations, it appeared that some sacrifice in theoretical performance was considered acceptable.

As time went on, however, it was found that a completely satisfactory solution for the deficiencies of hydrazine could not be found, at least through the incorporation of additives. It was also found that the use of hypergolic starting fluids and the use of hypergolic additives to the hydrocarbon fuels eliminated the extremely difficult engineering problems associated with trying to burn the hydrocarbon fuels with nitric acid.

When the work under this contract was started, the primary objective was to develop a hydrazine derivative which would have not only the theoretical performance of hydrazine but also would possess superior physical and chemical properties, particularly low freezing point and greater stability. On the other hand, since hydrazine at this time was still so strongly in the picture as a prospective fuel, some short-range efforts were included in this program to utilize the superior properties of hydrazine to enhance certain conventional fuels, such as aniline and alcohol, rendering them hypergolic, increasing their performance or improving other characteristics.

The investigations of hydrazine derivatives were directed toward maximum performance, coupled with low freezing point and adequate stability. In considering carbon-hydrogen substituted hydrazines, it was clear that maximum performance required a minimum number of carbon atoms substituted into the molecule and a maximum amount of hydrogen. On the other hand, greater energy content could be introduced by substituting highly endothermic groups such as acetylenic groups or strained rings. Methylhydrazine, therefore, should give higher performance than dimethylhydrazine and the methyl hydrazines in general should give higher performances than the corresponding ethyl hydrazines. First attention was naturally given then to the methyl hydrazines, which were the simplest to prepare. Subsequent efforts were directed towards the derivatives containing higher energy substituents such as 3-membered rings and acetylenic groups.

The properties of methylhydrazine and of unsymmetrical dimethylhydrazine (UDMH) aroused interest almost immediately, with most attention being given to UDMH. The latter, in addition to relatively high performance, possessed an excellent combination of properties such as low freezing point, stability, ease of handling, miscibility with other fuels, extremely small ignition delay even at very low

temperatures and excellent prospects for ultimate low cost of production.

As a result of this great interest, a program was undertaken under which several hundred pounds of methylhydrazine and UDMH were prepared for distribution to various agencies throughout the country, in order that a diverse testing program could be carried out.

The efforts to find hydrazine derivatives which retained fully the theoretical performance of hydrazine or which might even exceed that has resulted in a number of compounds containing relatively high energy groups. However, it is notable that such compounds tend to be considerably less stable and much more difficult to prepare. It would be difficult to conceive of any such compounds being manufactured at as low an ultimate cost as can be foreseen for UDMH. Furthermore, the amount of improvement of theoretical performance possible is strongly limited and at most might give 2 to 3% increase over that of UDMH. Consequently, because of the existence of UDMH and because of its excellent properties, the further advantages which might conceivably be gained through these higher energy derivatives of hydrazine are distinctly limited and it appears that such compounds would only be useful for special purposes such as additives to JP-4 in relatively small quantities to induce smooth ignition, combustion and shutdown when burned with nitric acid.

For some time now interest has developed in such additives. UDMH, as well as certain acetylenic hydrocarbons, for example, have been found effective in this respect when added in proportions of about 10% to JP-4. Presumably, both the chemical reactivity of these substances with nitric acid, as well as their energy content (they are endothermic compounds), contribute to this effect. It is reasonable, therefore, to assume that the acetylenic or strained ring derivatives of hydrazine may also be useful as additives to promote smooth combustion of JP-4 fuel.

The present report is intended to give only a summary of all previous work conducted under the contract. Detailed experimental accounts can be found in the previous technical reports. The last technical report (M-55-1-ONR) covered work performed up to June 30, 1955. Experimental work has been conducted up to October 31, 1955, however, and since these investigations are not included in any past technical report, they are described in greater detail in the present report. The work during this period included the isolation and characterization of trimethylene hydrazine, monopro-

pargyl hydrazine and N-methyl-N-propargyl hydrazine. Further experiments designed at new syntheses of ethylenehydrazine and N-isocyanides are described.

III. CONCLUSIONS

As a result of the investigations under this contract, it may be concluded that:

1. Hydrazine may be added to such conventional fuels as aniline, ethanol, methanol, isopropanol or furfuryl alcohol to produce combinations which are superior to the conventional fuel itself with respect to such properties as freezing point, theoretical performance and sensitivity to hypergolic ignition.

2. Methylhydrazine and UDMH give theoretical performances only slightly below that of hydrazine, but are superior to the latter with respect to freezing point, stability and sensitivity to hypergolic ignition.

3. UDMH offers, in addition to its remarkably great sensitivity to hypergolic ignition with nitric acid, an excellent combination of desirable propellant characteristics; that is, high theoretical performance, high thermal stability, miscibility with a broad range of solvents and low melting point. However, a eutectic solution of UDMH and methylhydrazine may offer special advantages since its melting point is much lower, $-80^{\circ}C$ ($-112^{\circ}F$), and its density, boiling point, theoretical performance and heat capacity will be somewhat higher,

4. All of the methylated hydrazines have properties which make them useful as rocket fuels, as additives to fuels and as hypergolic ignition agents. From the viewpoint of theoretical performance and logistics, methylhydrazine and UDMH are of greatest potential importance.

5. Methylhydrazine and UDMH offer excellent possibilities as monopropellants, particularly in view of their excellent physical properties and their relatively great stability.

6. The methyl hydrazines can be stored for extended periods of time, possibly indefinitely, without deterioration, under conditions of limited access of air.

7. The methyl hydrazines can be stored safely and without fear of deterioration or freezing over a wide range of

temperature.

8. Prolonged contact with a continually renewed air supply causes appreciable deterioration of methylhydrazine and UDMH, but the rate of oxidation is not rapid enough to prohibit the normal procedures required for storage, handling and transfer.

9. Methylhydrazine is similar to hydrazine in its sensitivity to rapid oxidation under catalytic influence. UDMH, trimethylhydrazine and tetramethylhydrazine are far less sensitive. Tetramethylhydrazine is practically unaffected by catalytic influence. The relative catalytic effects of copper and iron shift completely with increased methylation of hydrazine. The catalytic effects in dilute aqueous solution are different from those obtained with the anhydrous hydrazine derivatives.

10. Methylhydrazine and UDMH are probably more suitable as regenerative coolants in rocket engines than is hydrazine because under comparable experimental conditions it is much more difficult to detonate the vapors of methylhydrazine than those of hydrazine, and UDMH cannot be detonated at all.

11. The viscosities of the different methylated hydrazines decrease with increasing number of methyl groups as would be expected from theoretical considerations. The viscosities of the eutectic solution of UDMH and methylhydrazine fall between those of the individual components. Even at low temperatures all the methylated hydrazines retain comparatively low viscosities.

12. Methylhydrazine and UDMH are compatible with the important structural materials used for rocket engines and tanks and will not create difficult or new problems in this respect.

13. Combinations of hydrazine with methylhydrazine or UDMH may be used to secure even lower freezing points. However, only about 2.8% to 20.5% hydrazine by weight can be added to achieve these purposes.

14. Other hydrazine derivatives which have been prepared and which offer possibilities as fuels or additives for special purposes are ethylenehydrazine, 1,2-dimethyldiazetedine, trimethylenehydrazine, monopropargyl hydrazine, 1-propargyl-pyrazoline-3, N-methyl-N-propargyl hydrazine.

IV. SUMMARY OF WORK

A. Systems with Hydrazine.

The many excellent properties of hydrazine as a rocket fuel
may be conferred to more conventional fuels, at least in
part, by judicious blending. Any one or more of the follow-
ing properties may be imparted to a conventional fuel by
the addition of hydrazine: increased theoretical performance,
improved hypergolic ignition properties with nitric acid,
increased density, lower temperature of combustion, increased
heat capacity, lower vapor pressure, and lower freezing point.

The extent of these effects will, of course, depend on the
hydrazine concentration, which in turn is controlled by con-
siderations of miscibility and freezing point. In many cases
the combination of small improvements in individual proper-
ties may be of more practical value than any single improved
property considered by itself. For example, a small re-
duction in combustion temperature plus a small increase in
heat capacity and a small decrease in vapor pressure may
solve a difficult regenerative cooling problem.

Without actually calculating the theoretical performances
of the mixtures studied, it can safely be assumed that the
addition of about 20% hydrazine will be required to give an
appreciable increase, and 40% or more to give a significant
increase in the theoretical performance.

In accordance with the program under objectives A and B, the
phase relations of hydrazine with a number of more conven-
tional fuels have been investigated. In addition, various
other substances, selected for their possible effectiveness
as freezing point depressants, good propellant performance,
hypergolic ignition properties, or desirable logistics were
tested as third components. Ignition studies were made
with nitric acid and mixed acid, using a drop test technique
to obtain comparative values. The results of these tests
are given in Table XIII.

The following systems have been investigated:

1. Hydrazine-aniline
2. Hydrazine-aniline-methylamine
3. Hydrazine-aniline-ethylamine
4. Hydrazine-aniline-diethylamine
5. Hydrazine-aniline-triethylamine
6. Hydrazine-aniline-ethylenimine
7. Hydrazine-aniline-methanol

8. Hydrazine-aniline-ethanol
9. Hydrazine-aniline-ammonia
10. Hydrazine-aniline-acetylene
11. Hydrazine-furfuryl alcohol
12. Hydrazine-ethylenimine
13. Hydrazine-methanol
14. Hydrazine-ethanol
15. Hydrazine-methanol-ethanol-water
16. Hydrazine-acetonitrile-methanol
17. Hydrazine-isopropyl alcohol

As a result of this study, the solubility relations of hy-
drazine are better understood. A number of systems con-
taining hydrazine in solution with more conventional pro-
pellants, with or without third constituents, have been de-
veloped which freeze at -40°C or below, have excellent
hypergolic ignition properties with nitric acid, consist of
materials with good logistic characteristics, and possess
other advantages as rocket propellants, including: high
density, increased theoretical performance, ease of handling.
The significant results are summarized as follows:

1. Hydrazine and aniline form a eutectic mixture, which
freezes at -36°C and has the composition 17.3% by weight
hydrazine and 82.7% aniline. The observed results are given
in Table I, and a phase diagram plotted from these points is
shown in Figure No. 1. This composition possesses highly
improved hypergolic ignition properties with mixed acid and
with fuming nitric acid, as compared with aniline alone. It
ignited spontaneously with specially prepared solutions of
low concentration mixed acid and nitric acid which are too
dilute to ignite aniline at all. Ignition tests are given in
Table XIII. The freezing point of this system is raised by
small additions of water; e.g. 0.87% water brings the
freezing point to -29.2°C.

2. The freezing points of hydrazine-aniline mixtures are
depressed to -40°C or below by the addition of small quan-
tities of methylamine as a third component. For example, a
mixture containing 14.7% by weight hydrazine, 81.3% aniline,
and 4.0% methylamine freezes at -40°C. This mixture shows
much better ignition properties with WFNA than does pure
aniline and has approximately the same sensitivity to ig-
nition as the hydrazine-aniline eutectic mixture. The
freezing points of these ternary systems are also sensitive
to water, but some of the solutions can tolerate appreci-
able amounts of water and still retain a freezing point
below -40°C; e.g. 2.5% by weight of water added to a so-
lution containing 10% hydrazine, 80% aniline and 10% methyl-
amine raises the freezing point only to -41°C from -46°C.

Results of the experiments are given in Table II. These
data are plotted on a ternary diagram in Figure No. 2. In
order to construct this diagram, data from Tables I and II
were used, as well as some measurements on hydrazine-
methylamine mixtures (no aniline present) from reference
25. The latter measurements were made using 95.5% hydra-
zine.

The terminal points of the isothermals in the diagram are
determined values, but the lines drawn between these points
are roughed-in approximations. The $-36^\circ C$ and $-40^\circ C$ iso-
thermals are more accurately drawn, more data having been
accumulated for that range of temperatures.

3. Ethylamine and diethylamine used as third components
with the hydrazine-aniline system are found to give so-
lutions freezing below $-40^\circ C$. For example, a solution con-
taining 11.1% hydrazine, 75.7% aniline and 13.2% ethylamine
freezes at $-45^\circ C$; a solution containing 10% hydrazine, 75%
aniline and 15% diethylamine freezes at $-40.5^\circ C$. Triethyl-
amine was also tested as a third component. The lowest
freezing mixture obtained contains 10% hydrazine, 70% aniline
and 20% triethylamine and freezes at $-39^\circ C$. Results of these
determinations are given in Table III.

The ignition properties of these ternary systems with WFNA
are inferior to those of the eutectic hydrazine-aniline
mixture. They ignite with 98% nitric acid, but not with 96%
nitric acid, as does the hydrazine-aniline eutectic.

4. Additions of ethylenimine to hydrazine-aniline mixtures
bring the freezing points below $-40^\circ C$ and also improve the
hypergolic ignition properties with WFNA. For example, a
mixture containing 10.2% hydrazine, 75.3% aniline and 14.5%
ethylenimine freezes at $-45^\circ C$ and possesses somewhat better
hypergolic ignition properties with WFNA than does the hy-
drazine-aniline eutectic mixture. The freezing point of
this solution remains below $-40^\circ C$ even when 2% of water is
added to it.

In order to determine which mixtures of these three con-
stituents would give freezing points below $-40^\circ C$, a ternary
diagram was constructed (Figure No. 3) which is incomplete,
but adequate for choosing the range of compositions required.
The terminal points of the isothermals are determined points;
the tie-lines are roughed in approximately. Data for the
diagram were taken from Tables I and IV as well as from
Table VII, which contains freezing point data for the binary
system hydrazine-ethylenimine.

5. On the basis of the phase relations determined for hydrazine-methanol (see Table VIII and Figure No. 6) it would be expected that the addition of small quantities of methanol to the hydrazine-aniline system would depress the freezing point. Ethanol, however, does not appear promising in this respect, as judged from the hydrazine-ethanol phase diagram (see Table IX and Figure No. 7). To serve as an added guide in selecting suitable ternary compositions, the freezing points of several aniline-methanol and aniline-ethanol mixtures were determined. These results, as well as the freezing point data for a number of ternary mixtures, are given in Table V.

Methanol added to hydrazine-aniline mixtures brings the freezing point below -40°C. However, even a 10% addition of methanol renders the mixtures non-hypergolic with WFNA, although still hypergolic with mixed acid. Ethanol added as a minor component to the hydrazine-aniline system does not depress the freezing point below -40°C.

6. The eutectic hydrazine-aniline mixture absorbs only 3.6% by weight ammonia and 0.98% acetylene at ambient temperature and pressure, and the resulting effects on the freezing point and ignition properties are too slight to warrant any conclusions regarding these additives.

7. The addition of 26.0% by weight of hydrazine to furfuryl alcohol lowers the freezing point of the latter to -40.5°C. The ignition properties of this mixture are slightly superior to those of furfuryl alcohol alone. Additions of as much as 5% of water to this hydrazine-furfuryl alcohol solution depress the freezing point even further. The results of the freezing point experiments are given in Table VI. A freezing point curve prepared from these data is given in Figure No. 4.

8. Because of its own potential use as a high-performing propellant, ethylenimine was tested as a freezing point depressant with hydrazine. In these experiments 95% pure (Mathieson Chemical Corporation) hydrazine was used. The results are presented in Table VII. No attempt was made to determine the solidus.

These data are plotted on a curve shown in Figure No. 5. In this system freezing points below -40°C are reached with solutions containing 85% or more of ethylenimine. Since ethylenimine is itself a high-performing propellant, hypergolic with nitric acid, no great improvement in its properties is to be expected by the addition of a small quantity

of hydrazine. However, ethylenimine is useful as a third
component in ternary systems containing hydrazine.

9. A hydrazine-methanol mixture containing 45% by weight
hydrazine freezes at -45°C; when 40% hydrazine is present
the freezing point is -58°C. The freezing points of this
system are lowered when water is added. These results are
tabulated in Table VIII. A phase diagram plotted from the
data in Table VIII is shown in Figure No. 6. Some of the
points appear to be contradictory and cannot be fitted to
the curve; at this time it is not known whether these points
are experimental errors or whether more complex phenomena
are taking place (such as change of crystalline form or
appearance of a liquid phase). The doubtful areas are in-
dicated by dashed lines.

The phase diagram as drawn shows the appearance of a maximum
at a composition corresponding to $1N_2H_4:2CH_3OH$, and a con-
cealed maximum at the composition $N_2H_4:CH_3OH$. Compositions
containing 46% by weight of hydrazine or less freeze below
-40°C.

These mixtures ignite readily with mixed acid, but not with
WFNA which contains 2.0% or more of water.

10. The freezing points of the hydrazine-ethanol system
were determined by the methods already described. The ethanol
was anhydrous (refluxed over calcium oxide and distilled).
The results are given in Table IX.

A phase diagram plotted from these points is given in Figure
No. 7. A maximum appears at a point corresponding to the
composition $1N_2H_4:2C_2H_5OH$, but none is observed at the com-
position $N_2H_4:C_2H_5OH$, as with methanol. Mixtures containing
10% by weight hydrazine, or less, freeze below -40°C. The
lowest freezing mixture containing a greater amount of hy-
drazine is one with a composition of about 35% hydrazine
and 65% ethanol and freezing at -36°C.

11. In the attempt to increase the hydrazine content as
much as possible, while retaining a low freezing point,
some preliminary studies were made with water and ethanol
as additional components to the hydrazine-methanol system.

The data presented in Table X reveal the fact that additions
of water, or water in combination with ethanol, make possible
the preparation of mixtures containing more than 46% hydra-
zine, but still freezing below -40°C. For example, one
mixture contains 55.1% hydrazine and only 9.1% water, and

freezes at -44.0°C. Another mixture containing 50.1% hydrazine and only 4.1% water freezes at -40.5°C. Some of these solutions contain as much as 10% water but are hypergolic with 96.0% nitric acid.

12. A thermal analysis of the hydrazine-isopropyl alcohol system permitted construction of the freezing point curve. Solutions containing 20% or more hydrazine by weight froze above -40°C. The determined values are given in Table XI and a curve plotted from these data is given in Figure No. 8.

13. The results of freezing point determinations on several other systems containing hydrazine are given in Table XII. It is known that a small amount of ammonia can be dissolved in hydrazine at atmospheric pressure with a resulting small depression of the freezing point. The eutectic mixture of hydrazine and aniline, therefore, was saturated with ammonia at ambient temperature and atmospheric pressure in order to depress the freezing point below -40°C if possible. The result given in Table XII shows that the ammonia lowered the freezing point to -39.0°C. The addition of ammonia to the hydrazine-aniline system offers little advantage, since concentrations great enough to lower the freezing point below -40°C would produce pressures above atmospheric.

14. A hydrazine-aniline solution saturated with acetylene gas at ambient temperature and atmospheric pressure absorbed only 0.98% of the gas; and there was no appreciable change in the freezing point. The hydrazine-aniline solution used for this test was not exactly the eutectic mixture and froze at -34.0°C; the addition of acetylene affected no change.

15. When an equimolar quantity of acetonitrile is mixed with hydrazine, a drop in temperature of about 10°C occurs, indicating endothermic mixing. However, this solution shows liquid phase separation at -6.5°C. Methyl alcohol was added to increase the mutual miscibility of the liquids. The freezing points of the resulting solutions are shown in Table XII. An equimolar mixture of the three components freezes at -58.5°C.

16. Addition of ethyl alcohol as a fourth component to solutions of hydrazine-aniline-methylamine was found to lower the freezing points as indicated by the results in Table XII. From the few points measured it is not possible to determine the optimum compositions, but freezing points below -40°C were obtainable with relatively small quantities of methylamine and ethanol.

B. Methyl Derivatives of Hydrazine.

The investigation of hydrazine derivatives which would pos-
sess theoretical performances comparable to that of hydra-
zine while retaining superior physical and chemical charac-
teristics, was confined primarily to the substitution of
carbon-hydrogen groups. Although the maximum performances
would be achievable by the introduction of higher energy
groups such as acetylenic or strained-ring substituents,
the first approach adopted was the preparation of the methyl
derivatives of hydrazine, because they represented an ob-
jective quickly reached as well as a definite superiority
with respect to ultimate logistics.

The introduction of a methyl group would be expected to re-
duce the theoretical performance of hydrazine somewhat and
the introduction of succeeding methyl groups would be ex-
pected to reduce the performance even further. However,
the decrease in theoretical performance would be relatively
small and it was conceivable that actual performance results
might be comparable to those obtained with hydrazine. The
methylated derivatives, as fuels, would require optimum
mixture ratios with a considerably higher proportion of
oxidizer to fuel than does hydrazine, and this would be a
further advantage from the viewpoint of logistics and cost.
Most attention was given to methylhydrazine and unsymmetrical
dimethylhydrazine because they were the easiest to prepare
and were the most likely of the methyl derivatives to possess
the optimum combination of high performance and superior
physical and chemical properties. The investigations in-
cluded some development of synthetic methods, the determi-
nation of various physical properties, including stabilities
and other characteristics related to the use of these ma-
terials as rocket propellants. During the course of this
work, the evidence submitted to show the excellent qualities
of these materials as rocket fuels prompted the sponsoring
agency to appropriate some additional funds for the purpose
of manufacturing several hundred pounds of methylhydrazine
and unsymmetrical dimethylhydrazine for distribution to many
agencies throughout the country for test and evaluation
purposes. The work on the methylated hydrazines is summa-
rized below:

1. A study of the literature revealed that a number of
methods for the preparation of the various methyl hydrazines
is available, and some of these offer convenient synthetic
routes for the preparation of the compounds in the laboratory.
On the whole, none of these methods can be considered as
economically feasible, because of low yields, involved

manipulations, or expensive starting materials. Methods of preparing methylhydrazine are described in the following references (7, 10, 14, 16, 20, 28, 29, 30, 31, 32, 33, 35 and 36). Methods for the preparation of unsymmetrical dimethylhydrazine are given in the following references (6, 11, 13, 16, 19, 23, 26, 27 and 28). The following references contain procedures for the preparation of symmetrical dimethylhydrazine (12, 16, 17, 18, 24 and 31). The preparation of trimethylhydrazine is described in references 8 and 9. The preparation of tetramethylhydrazine is described in reference 9.

2. This laboratory has developed a method for the preparation of methylhydrazine and UDMH in good yields by the direct methylation of hydrazine with dimethylsulfate. The relative quantities of methylhydrazine and UDMH obtained can be varied by altering the mole ratios of dimethylsulfate to hydrazine. Small amounts of symmetrical dimethylhydrazine and trimethylhydrazine can also be obtained in this reaction. A comparison of the relative quantities of methylated derivatives formed in this reaction is given in Tables XIV and XV.

3. Good yields of methylhydrazine were obtained by a new process in which the neutral salt of hydrazine sulfate is directly methylated with dimethylsulfate. This procedure avoids the use of large excesses of hydrazine.

4. The methylation of symmetrical dimethylhydrazine by dimethylsulfate in accordance with the process developed in this laboratory results in quantitative yields of trimethylhydrazine based on the use of one methyl group per mole of dimethylsulfate.

5. The methylation procedure was employed to manufacture several hundred pounds of methylhydrazine and UDMH for distribution to various agencies for their test programs.

6. A process for the production of UDMH has been developed which involves the reaction of chloramine with dimethylamine. Yields as high as 75%, based on the chloramine consumed, have been obtained with this modified Raschig reaction.

7. A process for the reduction of N-nitrosodimethylamine in alkaline solution has been developed, using either zinc or aluminum. The latter gave yields as high as 85% to 90% for the reduction step.

8. Attempts to reduce N-nitrosodimethylamine at atmospheric pressure with hydrogen in the presence of various catalysts (nickel, platinum and palladium) have resulted in small yields of UDMH, but accompanied by large amounts of ammonia and dimethylamine which arose from the reduction of the N-N bond.

9. A new process has been developed for the preparation of tetramethylhydrazine, which involves the reaction of tri-methylhydrazine with formaldehyde and formic acid. Yields of 60% have been obtained.

10. A table summarizing the physical and thermochemical properties of the methyl hydrazines is given in Table XVI. These data are taken from the literature. Where references are not given, the data were determined in this laboratory.

11. The viscosities and densities of various methylated hydrazines over a wide range of temperatures were determined. The results of these measurements are given in Tables XVII, XVIII, XIX, XX and XXI. Plots of the viscosity data are given in Figure No. 9 and of the density data in Figure No. 10. Some of the values obtained at low temperature are:

COMPOUND	TEMPERATURE $^{\circ}$C	DENSITY GMS/ML	VISCOSITY CENTI-POISES
Methylhydrazine	-52.0	0.9433	13.319
UDMH	-55.0	0.8684	5.114
Eutectic solution of Methylhydrazine-UDMH	-60.0 -70.0	0.9033 0.9118	13.68 36.06
Trimethylhydrazine	-68.8	0.8683	6.643
Tetramethylhydrazine	-90.0	0.8799	5.359

12. Theoretical performances have been calculated by the exact method for the systems: methylhydrazine-liquid oxygen and uns-dimethylhydrazine-liquid oxygen, assuming a com-bustion chamber pressure of 300 psia and "frozen" equi-librium. The maximum specific impulse for methylhydrazine-liquid oxygen was found to be 261.9 lb-secs/lb at a mixture ratio of 1.10 (oxidizer/fuel, by weight); that for the system uns-dimethylhydrazine-liquid oxygen was found to be 260.0 lb-secs/lb at a mixture ratio of 1.25. Complete data

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are given in Tables XXII and XXIII. Results are plotted in
Figure No. 11.

13. The theoretical performances of the various methyl
hydrazines using RFNA (containing 15% NO_2) as oxidizer were
calculated by the short-cut method developed by Stewart A.
Johnston (Ref. 21). The values obtained were as follows:

	Specific Impulse, lb-secs/lb	
Fuel	Frozen Equilibrium	Shifting Equilibrium
Hydrazine	238	246
Methylhydrazine	237	246
UDMH	236	245
Sym-Dimethylhydrazine	236	245
Trimethylhydrazine	234	244
Tetramethylhydrazine	233	243

14. Theoretical performances were calculated for methyl-
hydrazine and UDMH as monopropellants in a rocket, assuming
decomposition to the elements, a combustion pressure of 300
psia, an exhaust pressure of 14.7 psia, and frozen equilib-
rium. The performance of methylhydrazine is 151.2 lb-secs/lb,
and that of UDMH is 137.3 lb-secs/lb. Theoretical con-
siderations, as well as experimental evidence, however,
show that the decomposition would be much more complex and
that probably appreciably higher performances would be
attainable.

15. No signs of deterioration were observed in samples of
methylhydrazine and UDMH which had been stored under nitrogen
for 48 days. No difference in stability was noted between
samples stored in daylight or in total darkness.

16. Comparative tests were performed on methylhydrazine,
UDMH and hydrazine to determine their relative stabilities
to oxidation by air. After bubbling air through these liquids
at ambient temperature for 8-9 hours, the following net de-
creases in concentration were noted:

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Methylhydrazine	12 to 13%
UDMH	5 to 6%
Hydrazine	1.4%

17. Tests designed to simulate unfavorable storage conditions in which access of air to the surface of the stored liquid is possible (as in containers which are not air-tight and "breathe" with changes of temperature) showed that methylhydrazine and UDMH are relatively stable to such conditions.

18. Methylhydrazine, maintained at a temperature of 87.5°C (189.5°F) under nitrogen for 10 hours, showed no significant degree of deterioration. Similarly, UDMH refluxed under nitrogen for 7 hours at its boiling point of 63.3°C (146°F) showed no appreciable deterioration.

19. Comparative tests of methylhydrazine, UDMH and hydrazine with various materials revealed that many substances which are able to catalyze violent decomposition of hydrazine or methylhydrazine in the presence of air have little or no effect on UDMH. For example, contact with an insulating variety of asbestos caused spontaneous ignition of hydrazine at the end of three minutes and ignition of methylhydrazine at the end of eight minutes, but when UDMH was contacted with this asbestos no ignition occurred and not even a temperature rise could be observed during a test period of 35 minutes. Results of experiments are presented in tables XXIV, XXV, XXVI, XXVII, XXVIII, XXIX and XXX.

20. Experiments designed to show the catalytic effects of iron and copper salts on anhydrous hydrazine derivatives in the presence of air showed a specific shift in catalytic influence with increased methylation. The attack on hydrazine was accelerated markedly by copper, but not by iron. Methylhydrazine was affected strongly by both copper and iron. UDMH, sym-dimethylhydrazine and trimethylhydrazine were strongly affected by iron, but only slightly by copper. Tetramethylhydrazine was not affected by either iron or copper. The experimental results are plotted in Figure No. 12.

21. The catalytic effects of iron and copper salts on the methylated hydrazines were investigated in dilute aqueous solutions in the presence of oxygen. Hydrazine, methylhydrazine, and sym-dimethylhydrazine showed appreciable

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rates of oxidation even with no catalyst added. UDMH, tri-
methylhydrazine and tetramethylhydrazine were not appre-
ciably affected in the absence of catalyst. Iron showed a
somewhat protective action with hydrazine, methylhydrazine
and sym-dimethylhydrazine; but it had a slight deteriorating
action with UDMH, trimethylhydrazine and tetramethylhydrazine.
Copper had a destructive effect on hydrazine, methylhydra-
zine, UDMH, trimethylhydrazine and to a slight extent on
tetramethylhydrazine. The deterioration of sym-dimethyl-
hydrazine with copper was not notably different from the
blank. Experimental results are plotted in Figure Nos. 13,
14 and 15.

22. Methylhydrazine vapor showed far less tendency to de-
tonate when exposed to a hot wire than did hydrazine under
corresponding experimental conditions. No detonation was
observed with methylhydrazine vapor until the wire had
reached white heat, and then the resulting detonation was
very mild and appeared to propagate but a limited distance
through the vapor. Hydrazine, in similar experiments, de-
tonated when the wire barely glowed red, and the resulting
explosion was violent and extended throughout the entire
vapor.

Uns-dimethylhydrazine, trimethylhydrazine, tetramethylhydra-
zine and the eutectic mixture of UDMH and methylhydrazine,
in identical experiments, could not be made to detonate at
all, even when the wire reached white heat and finally
fused.

23. Samples of stainless steel, iron, aluminum, Teflon and
polyethylene showed no signs of having been attacked after
31 days immersion in methylhydrazine. The methylhydrazine
also remained unaffected. Identical results were obtained
with uns-dimethylhydrazine in similar tests.

24. The depressant effect of methylhydrazine on the freezing
point of hydrazine was very small and only solutions con-
taining less than 20% by weight of hydrazine froze below
-40°C. However, a low-melting eutectic, freezing at -60°C
was formed at a composition containing about 12.4% hydrazine
by weight. Experimental data are presented in Table XXXI
and are plotted in Figure No. 16.

Uns-dimethylhydrazine was even less effective than methyl-
hydrazine in lowering the freezing point of hydrazine. So-
lutions containing more than about 7% of hydrazine froze
above -40°C. A eutectic freezing at -62.5°C was formed at
a concentration of about 3.2% hydrazine by weight. Experi-

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mental data are presented in Table XXXII and are plotted in Fig. No. 17.

25. Freezing point data were determined for the system methylhydrazine-water, but a large portion of the curve could not be characterized because of the tendency for solutions containing from 15% to 55% water to form viscous liquids or glassy solids which would not crystallize. Experimental data are presented in Table XXXIII and are plotted in Fig. No. 18.

On the other hand, it was found possible to construct a phase diagram for the entire composition range of the uns-dimethylhydrazine and water system. Three eutectics and two maxima were found. The lowest melting eutectic occurred at -62°C at a concentration of about 2.2% water by weight. One maximum point occurred at -31°C and in composition corresponded to a monohydrate. The other maximum, corresponding to a pentahydrate, was found at -29.5°C. Experimental data are presented in Table XXXIV and are plotted in Fig. No. 19.

26. The phase relations of the system methylhydrazine-uns-dimethylhydrazine were also determined. A eutectic, freezing at -80°C (-112°F), appeared at the composition: 39.8% methylhydrazine and 60.2% uns-dimethylhydrazine by weight. Experimental data are presented in Table XXXV and are plotted in Fig. No. 20.

27. Preliminary determinations of freezing points, made with combinations of methylhydrazine, uns-dimethylhydrazine and hydrazine, indicate that no solutions containing these three compounds and freezing below -40°C contained a greater proportion of hydrazine than did those binary mixtures of methylhydrazine and hydrazine which freeze below -40°C.

28. The range of different solvents in which hydrazine and its derivatives are miscible broadens greatly in going from hydrazine to methylhydrazine to uns-dimethylhydrazine. Uns-dimethylhydrazine is miscible with practically all types of liquids, including the aliphatic hydrocarbons. Methylhydrazine dissolves also in most solvents, but is only partially miscible with aliphatic hydrocarbons, such as hexane. The solubility of hydrazine is limited to the more polar solvents, such as amines and alcohols.

29. The approximate dissociation constants of the methylated hydrazines were determined by measurement of the hydrogen ion concentrations at the half-neutralization points. The order of decreasing basicity was found to be:

> Methylhydrazine
> Hydrazine
> Sym-dimethylhydrazine
> Uns-dimethylhydrazine
> Trimethylhydrazine
> Tetramethylhydrazine

Titration curves are plotted in Fig. Nos. 21, 22, 23, 24 and 25.

30. Drop tests with varying concentrations of nitric acid were conducted with hydrazine and with all the methyl hydrazines and it was found that all of the methylated hydrazines were superior to hydrazine in sensitivity to hypergolic ignition. UDMH was the most sensitive of the compounds tested. Results are given in Tables XXXVI and XXXVII. In another type of ignition test in which the fuel is diluted to different degrees in benzene or hexane and dropped into 100% nitric acid, methylhydrazine, UDMH and trimethylhydrazine showed similar behaviors. These results are shown in Table XXXVIII.

C. Other Derivatives of Hydrazine.

The substitution of alkyl groups into the hydrazine molecule results in a lowering of theoretical performance and the greater the amount of carbon introduced, the greater is the decrease. In order to achieve maximum performance in the carbon-substituted hydrazines, it is therefore desirable to introduce high energy groups such as acetylenic groups or strained rings. Another means of increasing the energy content would be to increase the nitrogen chain length; for example a triazane derivative. Efforts, therefore, were made toward the preparation and characterization of derivatives of the types mentioned.

1. Ethylenehydrazine (N-aminoethylenimine) was prepared by an adaptation of the Wenker method for the preparation of ethylenimine (Ref. 37). This synthesis was accomplished in the following steps:

    a. The reaction of ethylene oxide with hydrazine to form 2-hydroxyethylhydrazine;

    b. The reaction of 2-hydroxyethylhydrazine with sulfuric acid to produce first the sulfate salt and finally the ester, 2-hydrazinoethylsulfate; and

    c. The reaction of the latter with caustic to produce ethylenehydrazine. This process results in a relatively low yield of product which is difficult to purify. However, by special methods of purification, a pure product was obtained which boils at 92°C, has a melting point of -40.5°C and a density of 0.9714 gms/ml at 24°C.

Because of the low yields of ethylenehydrazine obtained by the modified Wenker method and the difficulties in purification, other methods of synthesis were investigated, as follows:

    a. Modifications of the Wenker method in which different solvents, bases and conditions of reaction were employed. Although yields of product were obtained in certain cases, none of the modified procedures were found to be superior to the method as originally applied.

    b. The reaction of ethylene bromide with hydrazine under varying conditions. The results were not encouraging.

    c. Attempts to nitrosate ethylenimine followed by reduction. Nitrosation of ethylenimine was attempted under varying conditions of temperature and solvent, employing such diverse nitrosating agents as sodium nitrite, butyl nitrite and nitrosyl sulfuric acid. Efforts were made to reduce, with lithium aluminum hydride, the minute quantities of product which were occasionally obtained, but only small quantities of iodate-reducing material were secured, at best, the amount being insufficient to isolate and identify.

    d. The reaction of ethylenimine with hydroxylamine-O-sulfonic acid has been used as a method of establishing nitrogen-nitrogen bonds to form hydrazine derivatives (Refs. 28 and 29). The procedure was applied to ethylenimine, but under mild conditions only ethylenimine or its dimer were recovered, and under more severe conditions only polymers were obtained.

    e. Modified Raschig reaction. Ethylenimine was reacted with chloramine under various con-

ditions, and from the reaction mixtures yields as high as 39%, based on iodate titration, were obtained. However, no ethylenehydrazine was actually isolated, and it is impossible to state definitely whether the monomeric ethylenehydrazine was present and was destroyed or polymerized under the conditions employed to isolate the product, or whether some compound other than ethylenehydrazine was initially produced.

f. Reactions of the toluene sulfonate ester of ethanolhydrazine. Efforts were made to employ the sulfonate ester of ethanolhydrazine in a manner analogous to the sulfate ester used in the Wenker process. No success was achieved.

g. Reactions of hydrazine with bis (2-chloroethyl) sulfate. Attempts were made to alkylate hydrazine with bis (2-chloroethyl) sulfate in order to obtain ethylenehydrazine directly in the presence of a sufficient quantity of caustic. No ethylenehydrazine could be isolated from the products of reaction.

h. Reactions of hydrazine with 2-chloroethyl-toluenesulfonate. Just as with bis (2-chloroethyl) sulfate, 2-chloroethyltoluene-sulfonate was used in an effort to secure 2-chloroethylhydrazine as an intermediate or ethylenehydrazine as the final product without isolation of the intermediate. The results were inconclusive.

i. The decomposition of aminotriazole. The crystalline compound 4-amino-1,2,4-triazole was prepared by heating formhydrazide. The triazole was reacted according to the Wolff-Kishner procedure (Ref. 22) with potassium hydroxide in the presence of a platinum catalyst and elevated temperature. A volatile iodate-reducing product was obtained, but was ultimately determined to be only a solution of hydrazine in water.

2. Attempts to prepare N,N-dimethyl-N',N'-ethylenehydrazine by the reaction of dimethylhydrazinoethylsulfate with

caustic were not successful; difficulties were encountered
in forming the ester intermediate.

3. Trimethylenehydrazine (N-aminoazetidine) was prepared
in the following steps: Azetidine was prepared in 8.8%
over-all yield by the reaction of 3-aminopropylsulfate with
caustic; the azetidine was nitrosated in 37% yield by the
reaction of azetidine with butyl nitrite in benzene; the
nitrosoazetidine was reduced to trimethylenehydrazine in
34% yield, based on iodate titration, by reaction of the
nitroso compound with lithium aluminum hydride in ether.
Isolation and purification of the material was accomplished
with some difficulty and with considerable losses. The
maximum purity obtained was 95%, based on acid and iodate
analysis. This material boiled at 108-109°C and had a
freezing point of -24°C. A sample was subjected to hydrogen,
carbon and nitrogen analysis and the following results were
obtained:

	Found	Calculated
C	49.29	49.97
H	12.33	11.18
N	35.31	38.85

Although these results do not show as close a check as would
be desired, it must be recognized that the material used
was only 95% pure to start with. Further work could not be
done because of the relatively small quantity obtained and
because of a strong tendency to polymerize to a viscous
material on standing.

4. Attempts were made to produce a N-chloro derivative of
trimethylhydrazine, which could be used as an intermediate
in the preparation of other derivatives, such as acetylenic
compounds. Sodium hypochlorite and t-butyl hypochlorite
were used as chlorinating agents. However, the active
chlorine content disappeared rapidly even at low temperatures.
Similar attempts with UDMH showed considerable quantities
of active chlorine present at low temperatures. Subsequent
reactions of the assumed N-chloro derivative were per-
formed in situ with sodium acetylide. Volatile products
possessing the iodate-reducing function, as well as non-
basic, non-reducing material, were found. This work was dis-
continued before conclusions could be drawn as to the results.

5. Mannich type reactions were performed with trimethylhydrazine, formaldehyde and acetylene, and similar reactions were also performed using vinylacetylene instead of acetylene. When acetylene was used, a volatile product was obtained which contained an acetylenic group, but no iodate-reducing function. With vinylacetylene apparently two different products were obtained. In both cases, the amounts of material obtained were too small for purification and identification. Larger-scale runs would be required in further work.

6. Trimethylhydrazine was reacted with methylmagnesium iodide to yield the corresponding magnesium-iodide derivative of trimethylhydrazine. Treatment of the latter with propargyl bromide yielded a reaction mixture from which no identifiable products could be obtained. This work was not pursued sufficiently to draw conclusions concerning its possible ultimate success.

7. Acetotrimethylhydrazide was reacted with phosphorous pentachloride in an attempt to obtain an ethinyl derivative. The aceto derivative was prepared by the reaction of acetic anhydride with trimethylhydrazine. Subsequent reaction with phosphorous pentachloride, intended to produce N-methyl-N-ethinyl-N',N'-dimethylhydrazine, evolved hydrochloric acid in the required quantity. Polymeric products, as well as volatile material, resulted, but no identifiable substances could be isolated.

8. Hydrazine was reacted with propargyl bromide to yield at least two distinct products. One corresponds to the composition of monopropargylhydrazine and the other to that of dipropargylhydrazine. The latter boils at 39 - 40°C/3mm, has a density of 0.9942 gms/ml at 25°C, freezes below -83°C and has a refractive index of 1.4910 at 25°C. This compound has been shown to be a cyclized derivative corresponding to the composition 1-propargyl pyrazoline-3.

The compound corresponding to the monopropargylhydrazine derivative constituted a fraction boiling at 41 - 41.8°C/10 mm. When the reaction was performed without a solvent or fixed base and in the presence of a large excess of hydrazine, very small quantities of this fraction could be obtained. Consequently, a different synthetic procedure was followed which consisted in reacting 4 moles of hydrazine with 1 mole of propargyl bromide in ether solution at low temperature, 5-10°C, over an extended period of time, 8 hours. In this case, there was a material produced which, after considerable fractionation, showed a purity of 99% and boiled at 47°C/9mm. This material had a freezing point

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of -73°C and a density of 0.9845 g/ml at 19.2°C. The com-
pound is soluble in benzene, but not in hexane. A carbon,
hydrogen and nitrogen analysis was performed on a sample
of this material and the following results were obtained:

	Found	Calculated
C	46.64	51.40
H	8.73	8.63
N	33.63	39.97

The results appear rather poor, implying a considerably
less pure material than indicated by acid and iodate ana-
lyses. In order to obtain a better check and at the same
time to determine whether the compound was actually pro-
pargylhydrazine or a cyclized derivative, a m-nitrobenzal-
dehyde derivative of the compound was prepared. A crys-
talline solid, melting at 77.5°C, was obtained. The for-
mation of this derivative was evidence that the product
was propargylhydrazine and not a cyclized derivative. A
carbon, hydrogen and nitrogen analysis was performed on
this derivative and the results obtained were as follows:

	Found	Calculated
C	58.83	59.11
H	4.68	4.46
N	20.98	20.68

These results indicate that the compound prepared is mono-
propargylhydrazine.

9. Methylpropargylhydrazine was prepared by adding propargyl
bromide over an 8-hour period to an ether solution of methyl-
hydrazine at a temperature of 10°C. The mole ratio of me-
thylhydrazine to propargyl bromide used was 3:1. A viscous
liquid layer was formed from which the upper ether layer was
separated. The final product was isolated from the ether
by fractionation. A product was obtained which, analysed by
acid titration, indicated a purity of 99.6% as methylpro-
pargylhydrazine. This product is a liquid with boiling

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point at 27°C/8mm, or 106°C at atmospheric pressure; its
density is 0.9105 at 19.2°C; its freezing point is -95.3°C.
The material turns yellow in the presence of only traces of
oxygen. A carbon, hydrogen and nitrogen analysis revealed
the following:

	Found	Calculated
C	56.44	57.11
H	9.54	9.59
N	32.09	33.30

These results imply that the purity was not quite as high as
indicated by the acid analysis. In order to determine whether
this product was really N,N-methylpropargylhydrazine as was
expected or whether a cyclized derivative was formed, a de-
rivative of m-nitrobenzaldehyde was prepared. The derivative
appeared as yellow needles with a melting point of 58.5°C.
This melting point is similar to that of m-nitrobenzaldehyde
itself, but a mixed melting point showed a big depression in
melting point. A carbon, hydrogen and nitrogen analysis was
performed on the m-nitrobenzaldehyde derivative with the
following results:

	Found	Calculated
C	61.69	60.82
H	5.28	5.10
N	20.38	19.35

These results indicate that the compound is indeed N,N-
methylpropargylhydrazine which was prepared. Although no
exact assay was made, indications are that yields of this
product in excess of 60% are obtained. The methylpropargyl-
hydrazine, though soluble in benzene, was found to be in-
soluble in hexane.

10. Propargylation of acyl derivatives of hydrazine was
employed in an effort to direct the course of substitution
of the propargyl group. Sym-dimethylhydrazine has been pre-
pared by the methylation of dibenzoyl or diformyl hydrazine.

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In a similar fashion it was believed possible to prepare
sym-dipropargylhydrazine. Furthermore, the alkylation of
acyl derivatives of hydrazine may permit other opportunities
to effect a directed substitution. The following experi-
mental efforts were made:

    a.   Propargylation of dibenzoylhydrazine. Diben-
         zoylhydrazine prepared in the usual manner was
         reacted in aqueous solution with propargyl
         bromide to obtain finally, after suitable work-
         up, white crystals melting at $134^{\circ}C$. An ele-
         mentary analysis showed that the compound ob-
         tained was monopropargyldibenzoylhydrazine
         rather than the dipropargyl derivative which
         had been expected. Various attempts at hydro-
         lysis of this material resulted only in po-
         lymerization and no propargylhydrazine could
         be recovered from the reaction mixture.

    b.   Propargylation of tetramethyloxalylhydrazine.
         Tetramethyloxalylhydrazine was prepared in high
         yield by the reaction of UDMH with diethyloxalate,
         the white crystalline product melting at $230^{\circ}C$.
         Propargylation of this substance gave small
         yields of a white crystalline compound melting
         at $158^{\circ}C$. Efforts to recover a propargylated
         hydrazine from this reaction product were un-
         successful.

11. Efforts to prepare 1,2-dimethyldiazetidine by the re-
action of ethylene bromide with sym-dimethylhydrazine re-
sulted at first in a crystalline solid, melting at 48.5 -
50.5°C and boiling at $184^{\circ}C$. It was subsequently shown
that this compound was 1,2-bis (N,N'-dimethylhydrazino)
ethane.

In order to obtain conditions more conducive to the for-
mation of the desired diazetidine derivative, considerably
greater dilution was employed and the mole ratio of ethylene
bromide to sym-dimethylhydrazine held at 1:1. Under the
conditions of this reaction, a 15.8% yield of the desired
1,2-dimethyldiazetidine was obtained. The compound is a
liquid boiling at 70.2 - 70.4°C; the freezing point is
-91.6°C to -88.8°C. The density was determined to be
0.8099 g/ml at 25°C and the index of refraction, n_D^{25}, is
1.4130. Evidence was obtained to show that this compound
actually had the structure of 1,2-dimethyldiazetidine.

12. The reaction of tetramethylhydrazine with either methyl

iodide or methyl bromide produced the corresponding penta-methylhydrazinium halide. It was found impossible to produce the diquaternary salt by introduction of another molecule of methyl halide. These compounds were subsequently treated with sodium borohydride under various conditions in order to obtain pentamethylhydrazinium borohydride. Only small yields of impure products were obtained.

13. UDMH was treated with chloroform and caustic in attempts to prepare an N-isocyanide. However, only methyl isocyanide was obtained as an identifiable product. Methylhydrazine in a similar reaction gives good yields of methyl isocyanide.

Further efforts to prepare an N-isocyanide derivative were made by reacting silver cyanide with N-chlordimethylamine. This reaction was performed under varying conditions in different solvents but it was not possible to isolate any product which could be identified as the desired N-isocyanide.

14. Trimethylhydrazine was reacted with chloramine in a modified Raschig reaction similar to that described earlier in this report for the preparation of UDMH. The objective was to prepare a triazane; i.e., N-amino, N-methyl-N',N'-dimethylhydrazine. Small quantities of product boiling higher than trimethylhydrazine were obtained but in quantity too small for purification and identification. Further work would be required to draw conclusions as to the results of this reaction.

15. Hypergolic ignition characteristics of the hydrazine derivatives were determined by two types of tests. In one test the fuel was added dropwise to 0.5 ml of nitric acid contained in a small cup. To determine whether hypergolic ignition took place, the number of drops added to produce ignition were recorded. The drops were added at intervals of about 1 second to a total of 12 drops. If no ignition took place at that time, it was recorded as being non-hypergolic. In order to make a comparative evaluation of different fuels, these tests were performed with nitric acids of different concentrations, varying from 70% up to 100% nitric acid contents. Results of these tests are shown in Tables XXXVI and XXXVII.

The other type of ignition test was in accordance with the procedure employed by the New York University research group (Ref. 15). The fuels were diluted to varying degrees in benzene or in hexane and added dropwise to a small quantity of 100% nitric acid contained in a cup. The

ratings of the fuels employed here are the same as those used
by NYU. Results of these tests are shown in Table XXXVIII.
On the basis of the latter tests, 1-propargylpyrazoline-3
and methylpropargylhydrazine are most effective as hypergolic
additives.

16. The theoretical performances of the various hydrazine
derivatives using RFNA (containing 15% NO_2) as oxidizer as
well as liquid oxygen, were calculated by the short-cut
method developed by Stewart A. Johnston (Ref. 21). Results
are given in Table XXXIX. Hypothetical compounds are
also included. The heats of formation of the compounds were
estimated in all cases (except for hydrazine and some of the
methyl hydrazines); the estimated heats of formation are
noted in the table. The results show that the introduction
of higher energy groups into hydrazine can increase the
theoretical performance above that of UDMH and even that of
hydrazine, but the theoretical increases are small.

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TABLE I

Freezing Points of Hydrazine-Aniline Solutions.

Composition of Mixture Weight Per Cent		Freezing Point °C	
Hydrazine	Aniline	Liquidus	Solidus
0.0	100.0	- 6.2	
5.0	95.0	-14.0	-18.5
9.9	90.1	-22.0	-36.0
15.0	85.0	-29.5	
16.0	84.0	-31.0	
16.8	83.2	-32.2	
17.2	82.8	-33.5	
17.3	82.7	-36.0	
17.4	82.6	-35.2	
18.5	81.5	-33.5	
19.7	80.3	-32.0	
25.0	75.0	-24.0	-36.5
30.0	70.0	-19.0	-37.0
50.0	50.0	- 8.0	-34.0
70.5	29.5	- 2.0	- 9.0
90.0	10.0		- 1.0
100.0	0.0	+ 1.4	

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TABLE II

Freezing Points of Hydrazine-Aniline-Methylamine Solutions.

Composition of Mixture Weight Per Cent			
Hydrazine	Aniline	Methylamine	Freezing Point °C
14.5	69.0	16.5	-31.0
15.0	71.4	13.6	-32.0
15.7	74.8	9.5	-33.0
15.3	73.1	11.6	-33.5
16.8	79.5	3.7	-35.0
15.8	75.1	9.1	-35.0
10.4	81.7	7.9	-38.8
14.7	81.3	4.0	-40.0
13.1	79.9	7.0	-43.0
10.0	80.0	10.0	-46.0
9.1	71.6	19.3	-50.0
0.0	93.2	6.8	-14.5
0.0	89.6	10.4	-21.0
0.0	81.1	18.9	-40.0

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TABLE III

Freezing Points of Hydrazine-Aniline Solutions with Ethyl-
Diethyl- and Triethylamines.

Composition of Mixture
Weight Per Cent

Hydrazine	Aniline	Ethylamine	Diethyl-amine	Triethyl-amine	Freezing Point °C
10.0	80.0	10.0			-33.5
15.0	75.0	10.0			-35.0
11.1	75.7	13.2			-45.0
15.0	65.0		20.0		-24.0
10.0	80.0		10.0		-35.0
10.0	75.0		15.0		-40.5
10.0	80.0			10.0	-31.0
15.0	70.0			15.0	-32.0
10.0	75.0			15.0	-34.0
8.0	72.0			20.0	-37.0
10.0	65.0			25.0	-38.0
10.0	70.0			20.0	-39.0

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TABLE IV

Freezing Points of Hydrazine-Aniline-Ethylenimine Solutions.

Composition of Mixture Weight Per Cent			
Hydrazine	Aniline	Ethylenimine	Freezing Point $^{\circ}$C
12.9	78.5	8.6	-43.0
11.9	75.4	12.7	-42.0
10.2	75.3	14.5	-45.0
	90.1	9.9	-16.8
	79.5	20.5	-36.0
	72.0	28.0	very viscous at -75°C; glassy solid at -96.5°C.
	65.8	34.2	very viscous at -75°C; still not solid at -100°C.

TABLE V

Freezing Points of Solutions Containing Hydrazine, Aniline, Methanol or Ethanol.

Composition of Mixture Weight Per Cent				
Hydrazine	Aniline	Methanol	Ethanol	Freezing Point $^{\circ}$C
15.6	74.1	10.3		-39.0
14.9	71.1	14.0		-41.0
14.0	67.0	19.0		-43.0
20.2	59.6	20.2		somewhat viscous at -50°C, glassy solid at -73.5°C, no crystallization
	90.2	9.8		-18.0
	80.3	19.7		-28.0
	70.4	29.6		-38.5
15.2	74.9		9.9	-38.0
13.8	71.1		15.1	-38.5
	90.0		10.0	-14.0
	80.1		19.9	-21.0
	70.2		29.8	-27.0
	61.0		39.0	-32.1
	50.5		49.5	-40.2

TABLE VI

Freezing Points of Hydrazine-Furfuryl Alcohol Solutions.

Composition of Mixture Weight Per Cent		
Hydrazine	Furfuryl Alcohol	Freezing Point °C
0.0	100	-29.0
9.9	90.1	becomes viscous at about -33.0, glassy solid at -80.0, no crystallization
19.9	80.1	becomes viscous at about -40.0, glassy solid at -81.0, no crystallization
24.0	76.0	no crystallization
26.0	74.0	-40.5
28.0	72.0	-35.0
30.0	70.0	-30.5
40.0	60.0	-17.0
50.1	49.9	-10.5
69.4	30.6	- 5.0
90.1	9.9	- 1.0

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TABLE VII

Freezing Points of Hydrazine-Ethylenimine Solutions.

Composition of Mixture
Weight Per Cent

Hydrazine	Ethylenimine	Freezing Point $^{\circ}$C
0.0	100	-74.5
10.8	89.2	-48.5
19.4	80.6	-34.0
26.6	73.4	-26.0
32.5	67.5	-22.2
37.6	62.4	-21.0
41.9	58.1	-19.5
45.8	54.2	-18.0
49.1	50.9	-17.5
52.1	47.9	-16.5
54.7	45.3	-15.2
64.3	35.7	-14.2
82.8	17.2	-12.5
100.0	0.0	- 5.0

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TABLE VIII

Freezing Points of Hydrazine-Methanol Solutions.

Composition of Mixture Weight Per Cent		Freezing Point °C	
Hydrazine	Methanol	Liquidus	Solidus
100	0.0	+ 1.4	
80.0	20.0	- 8.5	-27.0
60.1	39.9	-23.0	-50.0
50.2	49.8	-33.0	-63.0
45.6	54.4	-44.5	-51.2
42.6	57.4	-53.0	-63.0
40.2	59.8	-58.0	-63.0
39.0	61.0	-60.0	-63.5
38.8	61.2	-60.0	-63.0
38.3	61.7	-50.0	-63.0
36.1	63.9	-51.5	-61.0
35.5	64.5	-58.8	-61.8
34.9	65.1	-54.0	-61.0
34.5	65.5	-59.0	-62.0
33.6	66.4	-59.5	-63.0
33.0	67.0	-58.0	-61.0
32.1	67.9	-58.0	-60.0
20.1	79.9	-69.2	-71.0

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TABLE IX

Freezing Points of Hydrazine-Ethanol Solutions.

Composition of Mixture Weight Per Cent		Freezing Point °C	
Hydrazine	Ethanol	Liquidus	Solidus
100	0.0	+ 1.4	
95.0	5.0	- 1.0	- 5.0
94.9	5.1	- 1.5	- 7.0
90.0	10.0	- 3.0	- 7.0
86.4	13.6	- 3.0	- 8.0
85.1	14.9	- 3.0	- 9.0
77.6	22.4	- 5.2	-12.0
70.5	29.5	- 6.0	-19.0
60.3	39.7	-11.0	-37.0
41.8	58.2	-24.0	-36.5
35.6	64.4	-32.8	-35.0
35.3	64.7	-34.0	-36.0
35.0	65.0	-33.0	-34.0
32.0	68.0	-31.5	-35.0
31.1	68.9	-31.2	-34.2
30.9	69.1	-31.0	-34.0
30.5	69.5	-32.0	-36.0
28.5	71.5	-31.0	-32.0
25.9	74.1	-30.8	-32.2
25.8	74.2	-31.0	-32.0
20.1	79.9	-31.5	-38.0
14.6	85.4	-36.0	-65.0
8.3	91.7	-44.0	below-90
4.5	95.5	-54.0	below-100

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TABLE X

Freezing Points of Hydrazine-Methanol Solutions Containing Ethanol or Water.

Composition of Mixture Weight Per Cent				Freezing Point °C
Hydrazine	Methanol	Ethanol	Water	
54.9	35.1		10.0	-47.0
55.1	35.8		9.1	-44.0
55.5	36.2		8.3	-40.5
56.1	36.5		7.4	-38.0
57.7	37.5		4.8	-35.0
49.6	32.4	11.9	16.1	-45.5
50.1	32.7	13.1	4.1	-40.5
52.3	34.1	13.6		-28.5
56.2	36.5	7.5		-26.0
58.2	38.0	3.8		-24.0

TABLE XI

Binary System: Hydrazine-Isopropyl Alcohol
Freezing Point Data

Composition of Mixture
Weight Per Cent

Hydrazine	Isopropyl Alcohol	Freezing Point °C
0.0	100.0	-89.0
2.0	98.0	-89.0
4.3	95.7	-85.0
6.1	93.9	-82.0
8.3	91.7	-80.0
10.0	90.0	-78.0
15.1	84.9	-61.0
20.1	79.9	-39.5
30.1	69.9	-21.0
39.9	60.1	-11.5
50.1	49.9	- 7.0
60.1	39.9	- 5.2
64.8	35.2	- 4.0
69.8	30.2	- 4.0
72.4	27.6	- 2.5
80.4	19.6	- 3.0
89.9	10.1	- 1.0
100.0	0.0	+ 1.4

TABLE XII

Freezing Points of Various Solutions Containing Hydrazine.

N_2H_4	$C_6H_5NH_2$	NH_3	C_2H_2	CH_3CN	CH_3OH	CH_3NH_2	C_2H_5OH	Freezing Point °C
16.7	79.7	3.6						-39.0
17.8	81.2		0.98					-34.0
43.8				56.2				Liquid phase separation at -6.5°
41.7				53.4	4.9			-19.0
39.8				50.9	9.3			-22.5
36.1				46.4	17.5			-35.5
34.6				44.3	21.1			-39.0
30.2				39.6	30.2			-58.5
14.2	68.1					12.9	4.8	-38.0
13.8	66.1					12.6	7.5	-42.0
12.9	62.1					11.8	13.2	-46.0
9.4	73.7					7.1	9.8	-38.5

TABLE XIII

Hypergolic Properties of Hydrazine *

Composition of Fuel Weight Per Cent			Weight Per Cent of Nitric Acid Used						
Hydrazine	Aniline	Methylamine	100	98	96	94	92	90	85
100	-	-	-	-	-	2,3,2	-	-	3,3,3
-	100	-	b.i.	b.i.	n.i.	n.i.	-	-	-
17.3	82.7	-	2,2	3,4	3,3	n.i.	-	-	-
80.0	20.0	-	-	-	-	3,3,2, 2,2	-	-	-
14.7	81.3	4.0	2,2, 3	5,2, 4	4,3, 3	n.i.	-	-	-
13.1	79.9	7.0	1,2, 2	4,3, 2,4	3,2, 3	n.i.	-	-	-
-	93.2	6.8	n.i.	-	-	-	-	-	-
-	81.1	18.9	b.i.	n.i.	-	-	-	-	-
Hydrazine	Aniline	Ethylenimine							
-	-	100	-	-	-	1,1,1	-	-	2,1,1
12.8	78.5	8.7	3,3, 2	2,4, 2	5,4, 3,4	n.i.	-	-	-

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TABLE XIII (Cont'd)

Hypergolic Properties of Hydrazine

Composition of Fuel Weight Per Cent			Weight Per Cent of Nitric Acid Used						
Hydrazine	Aniline	Ethylenimine	100	98	96	94	92	90	85
10.2	75.3	14.5	-	-	1,1,2	4,2,3	b.i.	n.i.	n.i.
-	90.0	10.0	8,4,6	b.i.	n.i.	-	-	-	-
-	79.5	20.5	2,2,2	1,2,2	7,5,5	2,6,3,5	5,8,7	b.i.	n.i.
Hydrazine	Aniline	Ethyl Amine							
11.1	75.7	13.2	-	5,4,3	n.i.	n.i.	-	n.i.	n.i.
Hydrazine	Aniline	Diethyl Amine							
-	-	100	1,1	-	-	4,5,4	-	n.i.	-
10.0	75.0	15.0	2,2,2	2,1,3	n.i.	n.i.	-	-	-
10.0	70.0	20.0	5,3,6, 2,9,6,4	n.i.	-	-	-	-	-
Hydrazine	Aniline	Triethyl Amine							
-	-	100	1,1	-	-	1,1	-	1,2,2	b.i.
10.0	70.0	20.0	3,3,2	2,3,2	n.i.	-	-	-	-

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TABLE XIII (Cont'd)

Hypergolic Properties of Hydrazine

Composition of Fuel Weight Per Cent			Weight Per Cent of Nitric Acid Used						
Hydrazine	Aniline	Methanol	100	98	96	94	92	90	85
15.6	74.4	10.0	n.i.	-	-	-	-	-	-
-	80.3	19.7	b.i.	-	-	-	-	-	-

Hydrazine	Aniline	Ethanol	100	98	96	94	92	90	85
15.2	72.4	12.4	b.i.	n.i.	-	-	-	-	-

Hydrazine	Furfuryl Alcohol	100	98	96	94	92	90	85
-	100	-	-	-	-	-	3,3,2	b.i.
9.9	90.1	-	-	-	-	-	4,4,1	b.i.
20.0	80.0	-	-	-	-	-	3,3,4	b.i.
26.0	74.0	-	-	-	-	-	2,3,3	8,7,8

TABLE XIII (Cont'd)

Hypergolic Properties of Hydrazine

Composition of Fuel Weight Per Cent				Weight Per Cent of Nitric Acid Used						
Hydrazine	Methanol	Ethanol	Water	100	98	96	94	92	90	85
45.6	54.4	-	-	5,6,7	n.i.	-	-	-	-	-
54.9	35.1	-	10.0	4,4,4	4,4,4	5,5, 4,4	n.i.	-	-	-
49.6	32.4	11.9	6.1	5,5,4	5,6,6	5,5,5	b.i.	n.i.	-	-
35.0	-	65.0	-	-	-	-	-	-	4,7,5	b.i.
14.6	-	-	85.4	n.i.	-	-	-	-	-	-

Hydrazine	Aniline	Ammonia		100	98	96	94	92	90	85
16.8	80.2	3.0		3,3,3	n.i.	-	-	-	-	-

Hydrazine	Aniline	Methyl Amine	Ethanol	100	98	96	94	92	90	85
12.9	62.2	11.7	13.2	n.i.	n.i.	-	-	-	-	-

TABLE XIII (Cont'd)

Hypergolic Properties of Hydrazine

| Composition of Fuel Weight Per Cent | | | Tests with Mixed Acid No. 1 ** | | | |
Hydrazine	Aniline	Methanol	Ambient Temp.	0°C	-20°C	-40°C
-	100	-	n.i.	-	-	-
18.0	82.0	-	3,3	3,3	3,4	b.i.
35.0	65.0	-	2,1,3,1	2,1,3,3	2,3,2	4,4,3
33.2	61.8	5.0	4,3,2,3	1,4,1,2	3,3,3	b.i.
31.5	58.5	10.0	3,2,2	b.i.	n.i.	-
16.2	73.8	10.0	4,3,3,4	n.i.	n.i.	n.i.
50.0	-	50.0	4,3,2,2	5,2,2	4,4	b.i.

Hydrazine	Aniline	Acetonitrile				
31.5	58.5	10.0	4,4	4,4,4	b.i.	n.i.

Hydrazine	Aniline	Acetylene				
17.8	81.2	1.0	3,3	3,3	3,4	n.i.

TABLE XIII (Cont'd)

Hypergolic Properties of Hydrazine

Composition of Fuel Weight Per Cent

			Tests with Mixed Acid No. 1 **			
Hydrazine	Methanol	Acetonitrile	Ambient Temp.	0°C	-20°C	-40°C
34.6	21.1	44.3	7,9	-	-	-

			Tests with Mixed Acid No. 2 **			
Hydrazine	Aniline	Methylamine	Ambient Temp.	0°C	-20°C	-40°C
-	100	-	1,1,1	2,2,2	3,3,4	b.i.
17.4	82.6	-	1,1,1	2,2,1	3,2,2	3,3,4
15.1	72.2	12.7	2,3,2	-	-	5,4,6
-	89.6	10.4	4,4,3	-	-	5,1,1,2

Hydrazine	Aniline	Ethylenimine	Ambient Temp.	0°C	-20°C	-40°C
16.1	76.8	7.1	1,2,2,1	1,2,2	4,3,2	4,4,4

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TABLE XIII (Cont'd)

Hypergolic Properties of Hydrazine

| Composition of Fuel Weight Per Cent | | Tests with Mixed Acid No. 3 ** | | |
Hydrazine	Methanol	Ambient Temp.	-20°C	-30°C
40.0	60.0	4,2,5,2	3,4,4	b.i.
45.0	55.0	3,4,4,3	4,3,3	3,3,4

*   Numbers represent the number of drops of acid required to produce ignition. The letters b.i. indicate border-line ignition; n.i. indicates no ignition.

** Compositions of the mixed acids were as follows:

	#1	#2	#3
Nitric acid	78.8%	85.6%	83.8%
Sulfuric acid	14.8%	14.1%	14.0%
Water	6.4%	0.3%	2.2%

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TABLE XIV

METHYLATED HYDRAZINES IN FIRST DISTILLATE
BASED ON 6 MOLES DIMETHYLSULFATE

Mole Ratio: N_2H_4/Me_2SO_4	3.74	3.25	3.00	2.75	2.50
Total Weight Distillate Grams	315	240.5	220	191.2	131.9
Composition, weight %					
Trimethylhydrazine	1.0	1.7	2.0	4.1	9.9
Uns-dimethyl-hydrazine	37.6	48.2	52.4	54.8	64.4
Unspecified (b.p.64-81°C)	2.7	3.8	4.6	6.6	4.8
Sym-dimethyl-hydrazine	2.7	3.0	2.9	2.7	-
Methylhydrazine	56.0	43.3	38.1	31.8	20.9

TABLE XV

METHYLATION OF HYDRAZINE

"2nd. Step Distillate"
(6 Mole Experiments)

Mole Ratio N_2H_4/Me_2SO_4		Trimethyl-Hydrazine	UDMH	Symmetrical Dimethyl-Hydrazine	Methyl-Hydrazine	Hydrazine	Sum
3.74	Weight, gms	2.4	93.3	6.7	139.3	37.2	-
	N_2H_4, moles	0.032	1.552	0.111	3.023	1.161	4.718
	CH_3, moles	0.096	3.104	0.222	3.023	-	6.445
3.25	Weight, gms	3.6	99.2	6.2	89.2	20.4	-
	N_2H_4, moles	0.049	1.651	0.103	1.936	0.637	3.739
	CH_3, moles	0.147	3.302	0.206	1.936	-	5.591
3.00	Weight, gms	4.0	105.7	5.9	76.7	9.8	-
	N_2H_4, moles	0.054	1.759	0.098	1.664	0.306	3.575
	CH_3, moles	0.162	3.518	0.196	1.664	-	5.540
2.75	Weight, gms	7.0	94.5	4.6	54.8	7.5	-
	N_2H_4, moles	0.094	1.572	0.077	1.189	0.234	2.932
	CH_3, moles	0.282	3.144	0.154	1.189	-	4.769
2.50	Weight, gms	12.4	80.9	-	26.2	-	-
	N_2H_4, moles	0.167	1.346	-	0.569	-	2.082
	CH_3, moles	0.501	2.692	-	0.569	-	3.762

TABLE XVI

Physical and Thermochemical Properties of Hydrazine and Some of its Derivatives

	Hydrazine	Methylhydrazine	Uns-Dimethyl Hydrazine	Sym-Dimethyl Hydrazine	Trimethyl Hydrazine	Tetramethyl Hydrazine
Melting Point °C	2.0 (5)	-52.37 (1)	-57.2 (4)	-8.92 (2)	-73 (9)	-95.9
Boiling Point °C	113.5 (5)	87/745 (35)	62.5/717 (26)	80.0-80.2	59.8/760	74.3/760
Density, gms/ml	1.0140/15° (5)	0.8743/25°	0.7861/25°	0.8208/25.8°	0.7668/25°	0.7683/25°
Density vs. temperature	see footnote a. (5)	see Table XVII	see Table XVIII	-	see Table XX	see Table XXI
Vapor pressure, equation	see footnote b. (5)	see footnote c. (1)	see footnote d. (4)	see footnote e. (2)	-	-
Surface tension dyne-cm^{-1}	66.67/25° (5)					
Viscosity, centipoises	0.9049 (5)	see Table XVII	see Table XVIII	-	see Table XX	see Table XXI
Refractive Index, n_D	1.46444/35° (5)	-		-	1.4039/20°(9)	1.4040/20°(9)
Heat of Formation (liq.) 298.16°K cals/mole	12,000 (5)	13,109 (see footnote f.)	12,724 (see footnote f.)	13,531 (see footnote f.)	-	-
Heat Capacity, 298.16°K cals/mole-deg.	23.62 (5)	32.25 (1)	39.21 (4)	40.88 (2)	-	-

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TABLE XVI (Cont'd)

Physical and Thermochemical Properties of Hydrazine and Some of its Derivatives

	Hydrazine	Methylhydrazine	Uns-Dimethyl Hydrazine	Sym-Dimethyl Hydrazine	Trimethyl Hydrazine	Tetramethyl Hydrazine
Heat of Fusion, at melting point cals/mole	3025 (5)	2490.5±3 (1)	2407.4±1.5 (4)	3295.5±5 (2)	-	-
Heat of Vaporization 298.16°K cals/mole	10,700 (5)	9648 (1)	8366±4 (4)	9400±15 (2)	-	-
Entropy of Ideal Gas, at 760 mm 298.16°K, E.U.	57.01 (5)	66.61±0.20 (1)	72.82±0.20 (4)	74.39±0.2 (2)	-	-
Dipole Moment Debye Units	1.83-1.90 (5)	1.68±0.14 (34)	-	-	-	-

a. $1.0253 (1-0.00085t)$ = density

b. $\log P = 7.80687 - 1680.745/ (T + 227.74)$

c. $\log P = 7.88 \log T - 3146/ T + 31.746$ (the original article contains an error in the decimal place of one of the terms).

d. $\log P = -2717.132/T - 6.745741 \log T + 28.000194$

e. $\log P = -10.540 \log T - 3407.0/T + 39.352$

f. Calculated from heat of combustion data in reference 3 (the article from which the data were taken contains an error in that a molecular weight of 60.01 instead of 60.1 was employed in calculating the heats of combustion of UDMH and sym-dimethylhydrazine).

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TABLE XVII

DENSITIES AND VISCOSITIES OF METHYLHYDRAZINE

Temperature °C	Density Gms/ml	Absolute Viscosity (Centipoises)	Kinematic Viscosity (Centistokes)
25.0	0.8743	0.781	0.893
0.0	0.8966	1.347	1.503
-30.0	0.9182	3.467	3.776
-37.0	0.9246	4.821	5.214
-45.0	0.9319	7.279	7.811
-50.3	0.9382	11.673	12.442
-52.0	0.9433	13.319	14.119

TABLE XVIII

DENSITIES AND VISCOSITIES OF UNS-DIMETHYLHYDRAZINE

Temperature °C	Density Gms/ml	Absolute Viscosity (Centipoises)	Kinematic Viscosity (Centistokes)
25.0	0.7861	0.509	0.647
13.8	0.7968	0.601	0.754
10.0	0.8017	0.645	0.805
0.0	0.8123	0.783	0.964
-5.0	0.8176	0.878	1.074
-15.0	0.8278	1.108	1.338
-25.0	0.8376	1.462	1.745
-35.0	0.8483	2.026	2.389
-45.0	0.8578	3.078	3.588
-55.0	0.8684	5.114	5.889

TABLE XIX

DENSITIES AND VISCOSITIES OF THE EUTECTIC
SOLUTION OF METHYLHYDRAZINE-UDMH

Temperature °C	Density Gms/ml	Absolute Viscosity (Centipoises)	Kinematic Viscosity (Centistokes)
25.0	0.8211	0.617	0.751
10.0	0.8358	0.809	0.968
0.0	0.8454	1.004	1.188
-10.0	0.8552	1.299	1.519
-20.0	0.8650	1.743	2.015
-30.0	0.8747	2.489	2.846
-40.0	0.8844	3.866	4.371
-50.0	0.8940	6.607	7.390
-60.0	0.9033	13.68	15.14
-70.0	0.9118	36.06	39.55
-72.5	0.9160	49.97	54.55

TABLE XX

DENSITIES AND VISCOSITIES OF TRIMETHYLHYDRAZINE

Temperature °C	Density Gms/ml	Absolute Viscosity (Centipoises)	Kinematic Viscosity (Centistokes)
25.0	0.7668	0.389	0.507
10.0	0.7837	0.471	0.601
0.0	0.7948	0.553	0.696
-10.0	0.8060	0.668	0.829
-20.0	0.8173	0.843	1.031
-30.0	0.8280	1.096	1.324
-40.0	0.8385	1.524	1.818
-50.0	0.8488	2.291	2.699
-60.0	0.8591	3.802	4.426
-68.8	0.8683	6.643	7.651

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TABLE XXI

DENSITIES AND VISCOSITIES OF TETRAMETHYLHYDRAZINE

Temperature °C	Density Gms/ml	Absolute Viscosity (Centipoises)	Kinematic Viscosity (Centistokes)
25.0	0.7683	0.430	0.560
10.0	0.7835	0.519	0.663
0.0	0.7936	0.583	0.735
-10.0	0.8032	0.672	0.837
-20.0	0.8133	0.785	0.966
-30.0	0.8229	0.930	1.131
-40.0	0.8324	1.141	1.371
-50.0	0.8421	1.438	1.708
-60.0	0.8518	1.905	2.236
-70.0	0.8612	2.541	2.951
-80.0	0.8706	3.595	4.129
-90.0	0.8799	5.359	6.090

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TABLE XXII

THEORETICAL PERFORMANCE OF METHYLHYDRAZINE

Oxidizer: Liquid Oxygen

Chamber Pressure: 300 psia

Exhaust Pressure: 14.7 psia

Equilibrium during Expansion: Frozen

Ratio (Oxidizer/Fuel)	0.90	1.10	1.25
Combustion Temperature, $^\circ K$	2977	3250	3339
Exhaust Temperature, $^\circ K$	1597	1793	1864
I_{sp}, lb-secs/lb	259.6	261.9	259.9
Molecular Weight of Gas	17.293	18.730	19.626

Composition of gas in mole fractions

	0.90	1.10	1.25
H_2O	0.28448	0.35281	0.38059
H_2	0.29641	0.20130	0.15062
CO	0.17398.	0.15673	0.14202
CO_2	0.02356	0.03686	0.04730
N_2	0.19728	0.19216	0.18624
NO	0.00051	0.00285	0.00615
O_2	0.00009	0.00164	0.00678
O	0.00025	0.00237	0.00683
H	0.01801	0.03184	0.03578
OH	0.00542	0.02145	0.03769

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TABLE XXIII

THEORETICAL PERFORMANCE OF UNS-DIMETHYLHYDRAZINE

Oxidizer: Liquid Oxygen

Chamber Pressure: 300 psia

Exhaust Pressure: 14.7 psia

Equilibrium during Expansion: Frozen

Ratio (Oxidizer/Fuel)	1.10	1.25	1.33	1.40
Combustion Temperature, ^{O}K	3023	3221	3291	3336
Exhaust Temperature, ^{O}K	1621	1762	1814	1850
I_{sp}, lb-secs/lb	257.8	260.0	259.9	259.3
Molecular Weight of Gas	17.777	18.785	19.269	19.660

Composition of gas in mole
fractions

	1.10	1.25	1.33	1.40
H_2O	0.26144	0.30875	0.32700	0.33916
H_2	0.28865	0.22285	0.19360	0.17152
CO	0.25007	0.23409	0.22470	0.21622
CO_2	0.03164	0.04374	0.05051	0.05639
N_2	0.14060	0.13804	0.13617	0.13428
NO	0.00051	0.00176	0.00287	0.00404
O_2	0.00012	0.00093	0.00222	0.00408
O	0.00034	0.00170	0.00333	0.00526
H	0.02053	0.03152	0.03553	0.03789
OH	0.00610	0.01661	0.02409	0.03116

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TABLE XXIV

SENSITIVITY TO CATALYTIC EFFECTS IN AIR
VERMICULITE

Temperature °C

Time, Minutes	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	27	27	27
1	29	28	26.5
2	30	29	27
3	31	30	27
4	32.5	31	27
5	34	32	27
10	37	35.5	26
15	39	42	-
20	40.8	49.8	-
30	44	58.8	-
60	48	62	30
80	51	90	-
94	55	108	-
95	-	106	-
98	-	97	-
100	-	90	-

Ten mls. of the hydrazine compound were added to 50 mls.
of the vermiculite. None of the temperatures shown under
uns-dimethylhydrazine were above ambient temperature.

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TABLE XXV

SENSITIVITY TO CATALYTIC EFFECTS IN AIR
ASBESTOS (INSULATING VARIETY)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	31	29.5	30
1	33.5	33	30.5
2	37	34.5	30.5
3	39.5	-	-
7	Ignition at end of 3 minutes	-	29.5
8		46 Ignition at end of 8 minutes. Flame was smothered and thermometer replaced.	-
25	-	122	-
30	-	140	-
31	-	155	-
32	-	167	-
33	-	176	-
34	-	187	-
35	-	220	30

Ten mls. of the hydrazine compound were added to 50 mls. of the asbestos. None of the temperatures shown under uns-di-methylhydrazine were above ambient temperature.

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TABLE XXVI

SENSITIVITY TO CATALYTIC EFFECTS IN AIR
ASBESTOS (ACID WASHED)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	32	32	33
1	39	35	33
2	47	36	33
3	54	40	33
5	62	48	33
10	74	64.2	35
15	-	73	-
17	-	81	-
18	-	110	-
19	-	158	-
20	82	230	37
21 to 23	-	250	-
24	-	210	-
25	-	190	-
30	88	100	38
40	93	52	38
50	96	-	39
52	151	-	-
54	206	-	-
56	261	-	42

Ten mls. of the hydrazine compound were added to 50 mls. of
the asbestos.

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TABLE XXVII

SENSITIVITY TO CATALYTIC EFFECTS IN AIR
MAGNESIA (85% MAGNESIA - 15% ASBESTOS)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	32	31	31
1	32.5	32	29
2	34	33	28
3	35	40	27.5
5	-	47	27
7	-	53	27
8	-	58	27
		Ignition after 8 minutes.	
10	41.5		-
15	42.2		-
20	41		-
25	39		27
	Ignition After 25 Minutes.		

Ten mls. of the hydrazine compound were added to 50 mls. of the magnesia. None of the temperatures shown under uns-di-methylhydrazine were above ambient temperature.

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TABLE XXVIII

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

ASBESTOS (LOW IRON)

Time, Minutes	Temperature $^{\circ}C$		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	32	31	31
2	37	36	-
5	51	49.5	32
8	60	-	-
	Ignition After 8 Minutes		
10	-	68	35
13	-	76	-
		Ignition after 13 minutes	
15	-	-	40
20	-	-	36

Ten mls. of the hydrazine compound were added to 50 mls. of the asbestos.

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TABLE XXIX

SENSITIVITY TO CATALYTIC EFFECTS IN AIR
GLASS WOOL (INSULATION GRADE)

Time, Minutes	Temperature °C		
	Hydrazine	Methylhydrazine	Uns-Dimethylhydrazine
0	28	28	28
5	29	32	24
10	30	35	24
15	31	38	24
20	34	43	24
25	35	49	24
30	36	55	25
40	38	74	26
45	38	79	26

Ten mls. of the hydrazine compound were added to 50 mls. of
the glass wool. None of the temperatures shown under uns-
dimethylhydrazine were above ambient temperature.

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TABLE XXX

SENSITIVITY TO CATALYTIC EFFECTS IN AIR

Comparison of Pyrex Glass Wool (Laboratory Grade) vs. Glass
Wool (Insulation Grade) using only Methylhydrazine

Time, Minutes	Temperature $^\circ$C	
	Pyrex Glass Wool	Glass Blowing Wool
0	26	26
5	30	29.5
10	46	34.5
20	62	48
30	71	76
35	71	83
40	72	79
50	73	69
55	71	58
60	69	53.5

Ten ml. quantities of methylhydrazine were added to 50 ml.
volumes of the respective glass wool samples.

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TABLE XXXI

Binary System: Methylhydrazine-Hydrazine
Freezing Point Data

Composition of Mixture
Weight Per Cent

Methylhydrazine	Hydrazine	Freezing Point $^{\circ}C$
0.0	100.0	+ 1.0
14.6	85.4	- 2.5
33.1	66.9	- 9.0
69.9	30.1	-29.0
84.3	15.7	-48.5
85.0	15.0	-50.5
86.5	13.5	-56.0
88.0	12.0	-59.5
88.5	11.5	-59.0
89.8	10.2	-59.0
92.6	7.4	-56.0
94.9	5.1	-54.0
96.8	3.2	-54.5
100.0	0.0	-52.5

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TABLE XXXII

Binary System: Uns-Dimethylhydrazine-Hydrazine

Freezing Point Data

Composition of Mixture
Weight Per Cent

Uns-Dimethylhydrazine	Hydrazine	Freezing Point $^{\circ}$C
0.0	100.0	+ 1.4
10.0	90.0	- 0.5
20.0	80.0	- 3.0
29.7	70.3	- 5.0
36.0	64.0	- 4.8
39.7	60.3	- 5.0
40.3	59.7	- 4.5
49.3	50.7	- 6.0
60.0	40.0	- 8.0
69.9	30.1	-10.5
80.0	20.0	-15.5
83.3	16.7	-20.0
84.1	15.9	-21.2
85.2	14.8	-24.5
92.2	7.8	-39.5
94.4	5.6	-47.5
95.0	5.0	-49.5
96.0	4.0	-58.5
96.4	3.6	-59.5
96.7	3.3	-59.0
97.9	2.1	-59.0
98.0	2.0	-59.5
100.0	0.0	-57.0

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TABLE XXXIII

Binary System: Methylhydrazine-Water
Freezing Point Data

Composition of Mixture Weight Per Cent		Freezing Point °C	
Methylhydrazine	Water	Liquidus	Solidus
29.8	70.2	-19.0	-84.0
34.9	65.1	-25.0	-86.0
40.2	59.8	-32.5	-84.0
44.9	55.1		
49.6	50.4		
55.9	44.1		
60.2	39.8		
64.9	35.1		
70.0	30.0		
75.2	24.8		
80.6	19.4		
85.4	14.6		
88.2	11.8		
94.3	5.7	-60.0	-78.0

These solutions became viscous between -20° and -40°C and formed glassy solids at about -80° to -86°C. No crystallization could be induced.

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TABLE XXXIV

Binary System: Uns-Dimethylhydrazine-Water
Freezing Point Data

Composition of Mixture
Weight Per Cent

Uns-Dimethylhydrazine	Water	Freezing Point $^{\circ}$C
10.0	90.0	- 3.2
21.2	78.8	-13.0
25.0	75.0	-19.5
26.9	73.1	-23.5
30.0	70.0	-29.5
30.0	70.0	-31.5
31.9	68.1	-35.0
36.0	64.0	-31.0
38.0	62.0	-29.8
40.0	60.0	-29.5
45.3	54.7	-29.7
45.9	54.1	-31.5
55.0	45.0	-35.5
55.3	44.7	-35.0
60.0	40.0	-42.5
62.0	38.0	-41.0
62.5	37.5	-40.7
64.5	35.5	-38.7
66.0	34.0	-37.0
70.0	30.0	-33.3
70.4	29.6	-33.5
77.2	22.8	-31.0
79.8	20.2	-31.5
90.3	9.7	-39.0
96.4	3.6	-55.0
97.5	2.5	-60.5
100.0	0.0	-57.0

TABLE XXXV

Binary System: Uns-Dimethylhydrazine-Methylhydrazine
Freezing Point Data

Composition of Mixture Weight Per Cent		Freezing Point °C	
Methylhydrazine	Uns-Dimethylhydrazine	Liquidus	Solidus
0.0	100.0	-57.0	-
19.4	80.6	-68.0	-71.5
36.0	64.0	-77.0	-80.0
41.0	59.0	-78.5	-80.0
50.9	49.1	-71.5	-80.0
61.5	38.5	-65.8	-74.0
76.1	23.9	-60.0	-64.0
100.0	0.0	-53.0	-

TABLE XXXVI

Hypergolic Properties of Hydrazine Derivatives

Temperature	Ambient				-40°C				-60°C
Weight Per Cent of Nitric Acid	85%	80%	75%	70%	85%	80%	75%	70%	90%
Fuel									
Hydrazine	3,3,3	-	-	n.i.	-	-	-	-	3,3,3
Methylhydrazine	1,1,1	-	-	n.i.	-	-	-	-	2,3,3,3,2
Sym-Dimethylhydrazine	2,1,1	-	-	n.i.	-	-	-	-	-
Uns-Dimethylhydrazine	1,1,1	-	-	1,1,1	-	-	-	-	1,1,1
Eutectic Solution of Methylhydrazine-UDMH	-	1,1,1	1,1,1	3,2,2	1,1,1	1,3,2	-	-	1,1,1
Trimethylhydrazine	-	-	1,1,1	2,2,2	-	1,1,1	3,2,2	-	1,1,1
Tetramethylhydrazine	-	1,1,1	1,2,2	5,4,4	1,1,1	1,1,2	2,1,1	n.i.	n.i.
Ethylenehydrazine	-	-	-	-	-	-	-	-	1,1,1
Propargylhydrazine	3,3,3	n.i.	n.i.	n.i.	-	-	-	-	-
Methylpropargylhydrazine	-	1,1	1,1,1,1	1,1,6,6	-	-	-	-	-

TABLE XXXVII

Hypergolic Properties of Hydrazine Derivatives

Composition of Fuel Weight Per Cent		Weight Per Cent of Nitric Acid							
		100	98	96	94	92	90	85	70
UDMH	**Aniline**								
10	90	-	6,4,4	3,3,4	n.i.	-	-	-	-
20	80	-	-	-	-	-	-	10,10,10	-
UDMH	**Ethanol**								
10	90	n.i.	-	-	-	-	-	-	-
20	80	n.i.	-	-	-	-	-	-	-
30	70	n.i.	-	-	-	-	-	-	-
35	65	7,8,7	6,10,4,7	-	8,4,8,7	6,4,5	-	4,4,4	n.i.
UDMH	**Furfuryl Alcohol**								
10	90	-	-	-	-	7,6,7	9,4,7	5,8,10	-
20	80	-	-	-	-	-	-	4,5,5	5,5,5
UDMH	**Ammonia**								
25	75	-	-	-	-	-	-	1,1,1	n.i.
75	25	-	-	-	-	-	1,1,1	-	1,1,1

TABLE XXXVII (Cont'd)

Hypergolic Properties of Hydrazine Derivatives

Composition of Fuel Weight Per Cent			Weight Per Cent of Nitric Acid							
UDMH	**Gasoline**		100	98	96	94	92	90	85	70
10	90		n.i.	–	–	–	–	–	–	–
15	85		n.i.	–	–	–	–	–	–	–
20	80		n.i.	–	–	–	–	–	–	–
23	77		10,3,7	–	–	–	–	–	–	–
25	75		5,5,5	–	12,10,12	–	–	–	–	–
28	72		2,3,4	–	10;9,10	10;10,9	–	–	–	–
UDMH	**Mixed Butyl Mercaptans**									
20	80		–	–	–	–	–	–	–	2,2,2

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TABLE XXXVIII

Ignition Tests with Nitric Acid

	Rating	
Fuel	In Benzene	In Hexane
Methylhydrazine	9	-
UDMH	9	6
Trimethylhydrazine	9	6
Tetramethylhydrazine	6	-
Ethylenehydrazine	7	-
1,2-dimethyldiazetidine	6	-
Monopropargylhydrazine	6	-
1-propargylpyrazoline-3	11	-
Methylpropargylhydrazine	11	-

Significance of Ratings

Ratings (See Ref. 15)

6. Hypergolic with 100% WFNA as a 35% solution in
    the diluent but not as a 25% solution.

7. Hypergolic with 100% WFNA as a 25% solution in
    the diluent but not as a 20% solution.

8. Hypergolic with 100% WFNA as a 20% solution in
    the diluent but not as a 15% solution.

9. Hypergolic with 100% WFNA as a 15% solution in
    the diluent but not as a 12.5% solution.

10. Hypergolic with 100% WFNA as a 12.5% solution in
    the diluent but not as a 10% solution.

11. Hypergolic with 100% WFNA as a 10% solution in
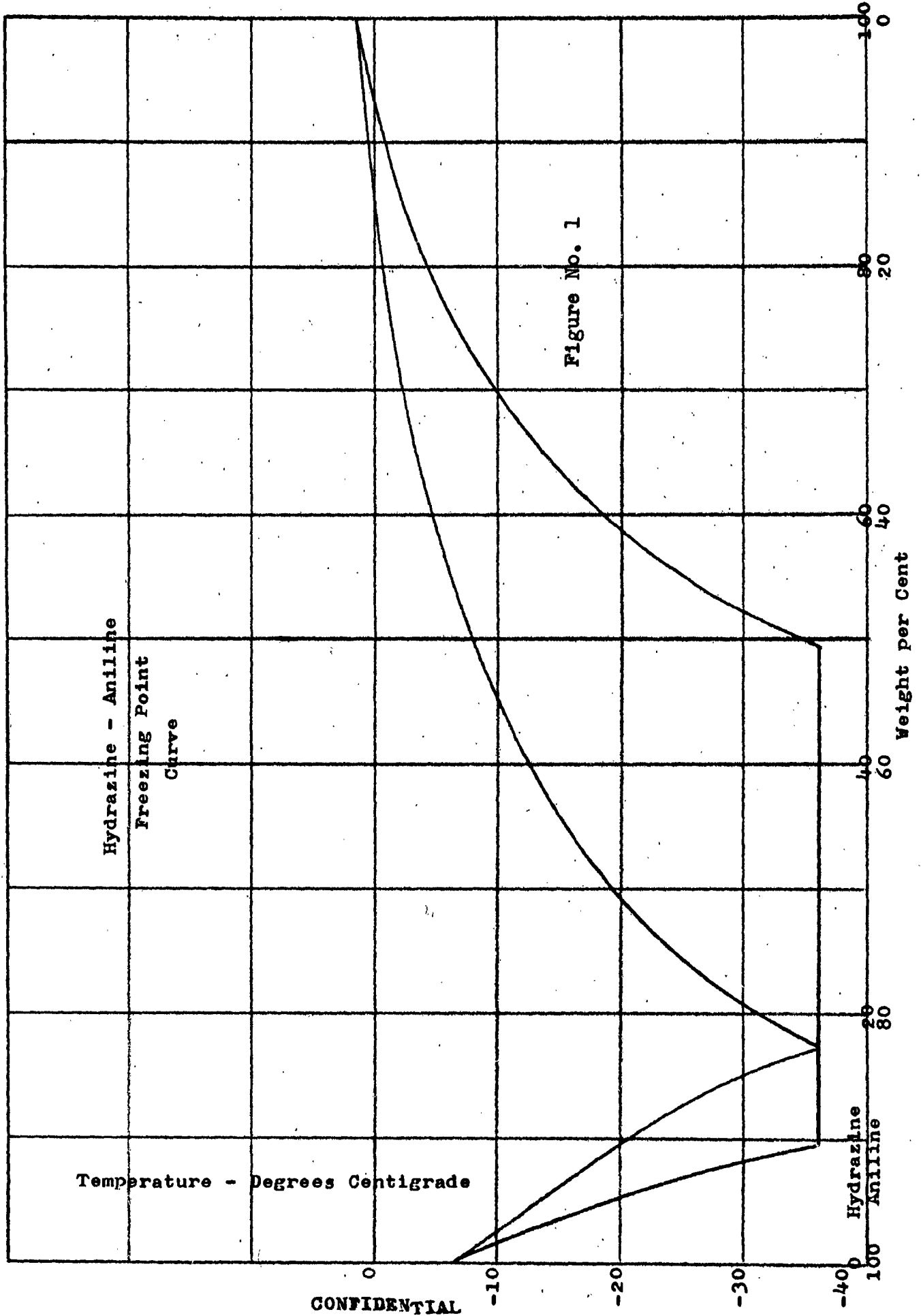   the diluent but not as a 7.5% solution.

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TABLE XXXIX

Theoretical Performances

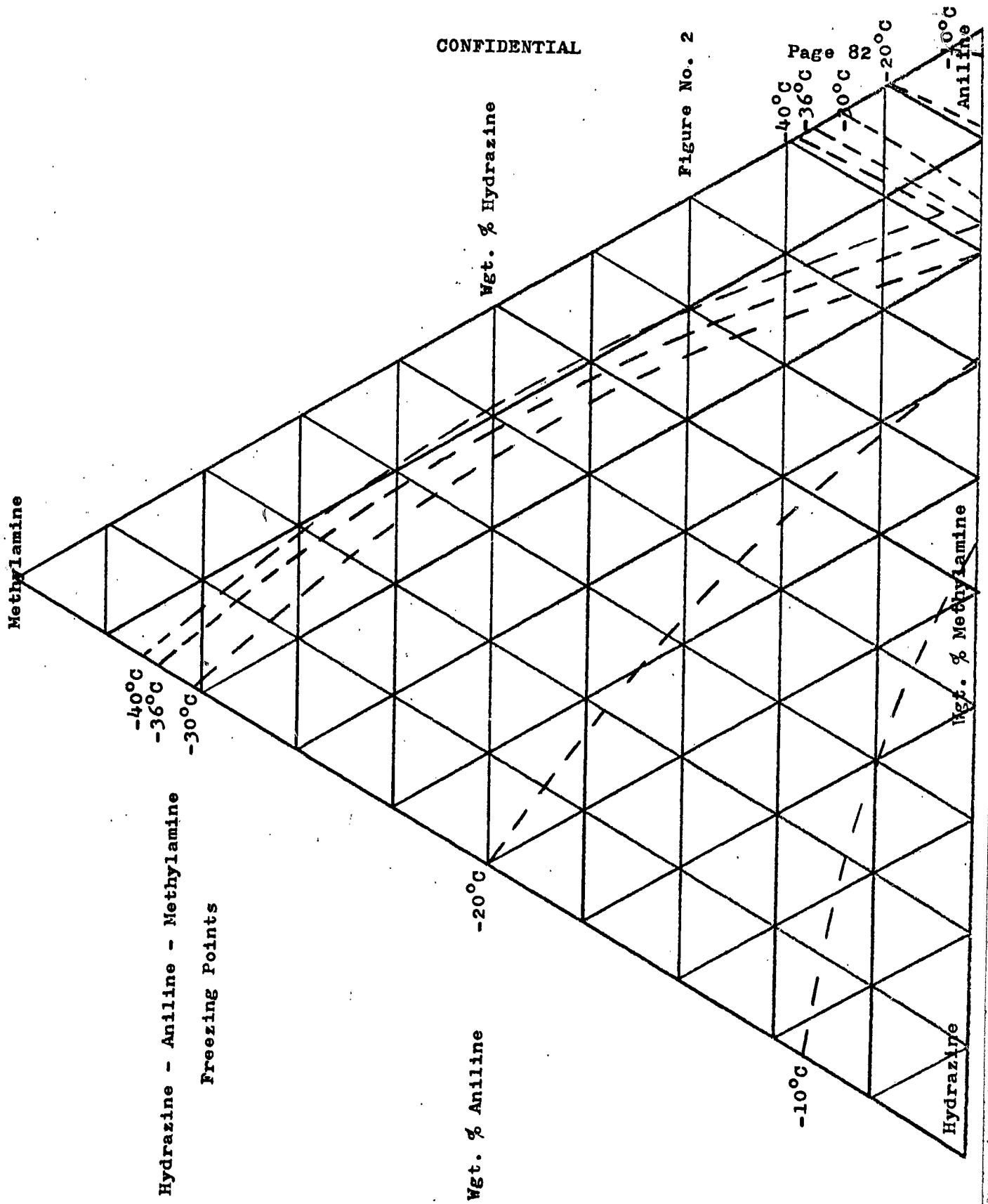Using RFNA (with 15% NO$_2$) and Liquid
Oxygen as Oxidizers

Fuel	Heat of Formation of Liquid	Liquid Oxygen Shifting Equilibrium	Specific Impulse lb-secs/lb. RFNA (with 15% NO$_2$)	
			Frozen Equilibrium	Shifting Equilibrium
Hydrazine	12.0	274	238	246
Methylhydrazine	13.11	272	237	246
UDMH	12.72	270	236	245
Sym-Dimethylhydrazine	13.53	270	236	245
Trimethylhydrazine	(14.9)	270	234	244
Tetramethylhydrazine	(16.1)	269	233	243
Ethylenehydrazine	(50)	275	238	251
Trimethylenehydrazine	(23.3)	266	231	241
Monopropargylhydrazine	(79.5)	275	237	252
Methylpropargylhydrazine	(81)	273	235	249
1,2-dimethyldiazetidine	(32.5)	268	231	242
(Trimethyltriazane)	(43.3)	273	(237)	(248)
N,N'-diethylenehydrazine	(94)	276	237	252
(N-Carbylaminodimethyl-amine)	(60.5)	270	(233)	(246)
1-propargylpyrazoline-3	(118.1)	270	233	248

Calculations were made by the short method developed by S. Johnston
(Ref. 21). Heats of formation in parentheses are estimated values.
Fuels given in parentheses are hypothetical and have not been
successfully prepared as yet.

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Hydrazine - Aniline
Freezing Point
Curve

Figure No. 1

Weight per Cent

Temperature - Degrees Centigrade

Hydrazine - Aniline - Methylamine

Freezing Points

Hydrazine-Aniline-Ethylene Imine
Freezing Points

Figure No. 3

Hydrazine - Furfuryl Alcohol
Freezing Point
Curve

Figure No. 4

Weight Per Cent

Temperature - Degrees Centigrade

Hydrazine - Ethylenimine
Freezing Point
Curve

Figure No. 5

Temperature - Degrees Centigrade

Weight Per Cent

Hydrazine - Methanol
Freezing Point
Curve

Figure No. 6

Hydrazine - Ethanol
Freezing Point
Curve

Figure No. 7

Weight Per Cent

Temperature - Degrees Centigrade

Hydrazine-Isopropyl Alcohol
Freezing Point Curve

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Figure No. 8

Weight Per Cent

Temperature - Degrees Centigrade

VISCOSITIES OF METHYLATED HYDRAZINES

FIGURE NO. 9

A - Methylhydrazine
B - Eutectic Solution Methyl-
    hydrazine-UDMH
C - UDMH
D - Trimethylhydrazine
E - Tetramethylhydrazine

Temperature °C

Viscosity in Centipoises

FIGURE NO. 10

DENSITIES OF METHYLATED HYDRAZINES

A – Methylhydrazine
B – Eutectic Solution Methyl-
hydrazine–UDMH
C – UDMH
D – Trimethylhydrazine
E – Tetramethylhydrazine

Density Gms/Ml

Temperature °C

Theoretical Performance Curves
Methylhydrazine, Uns-Dimethylhydrazine
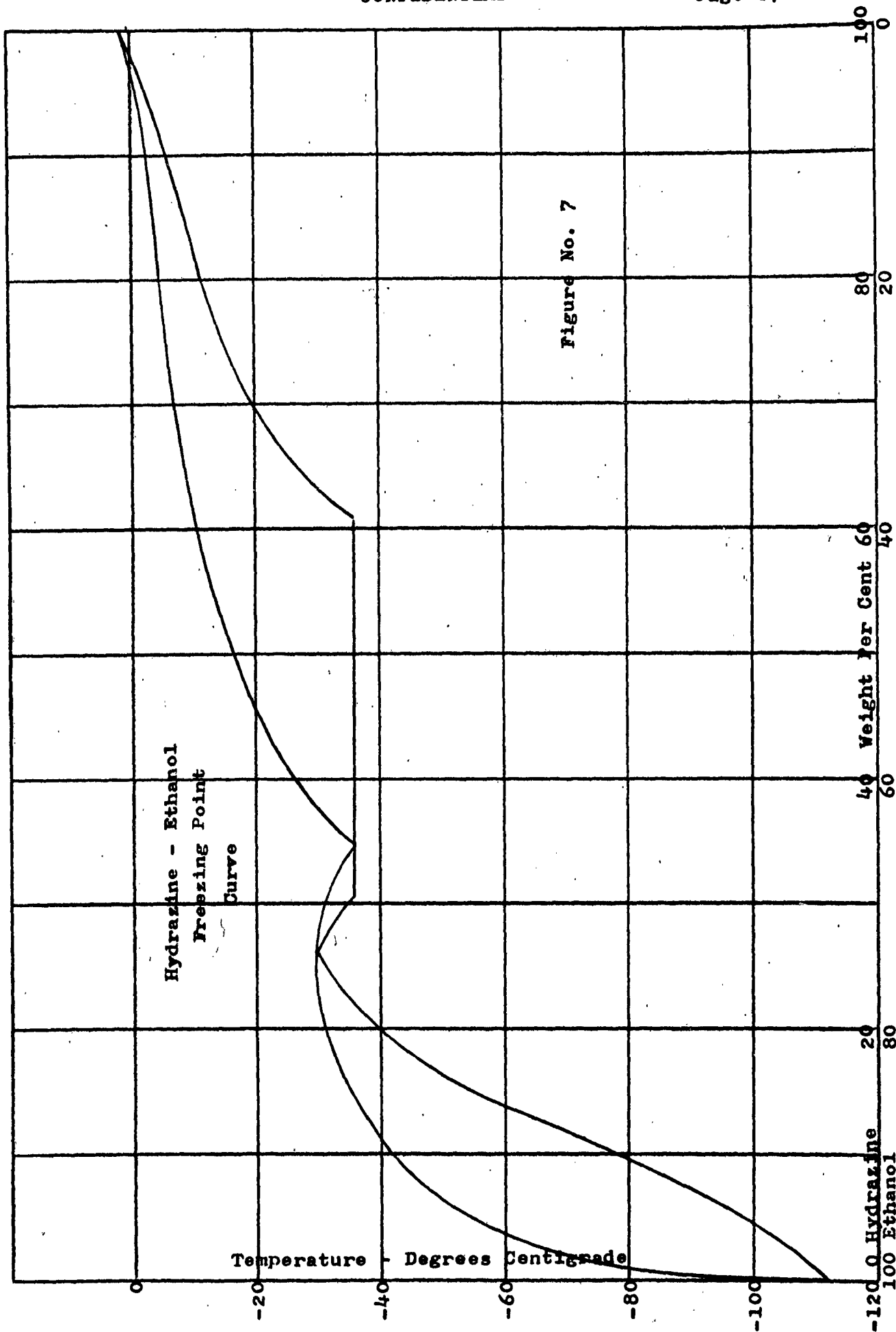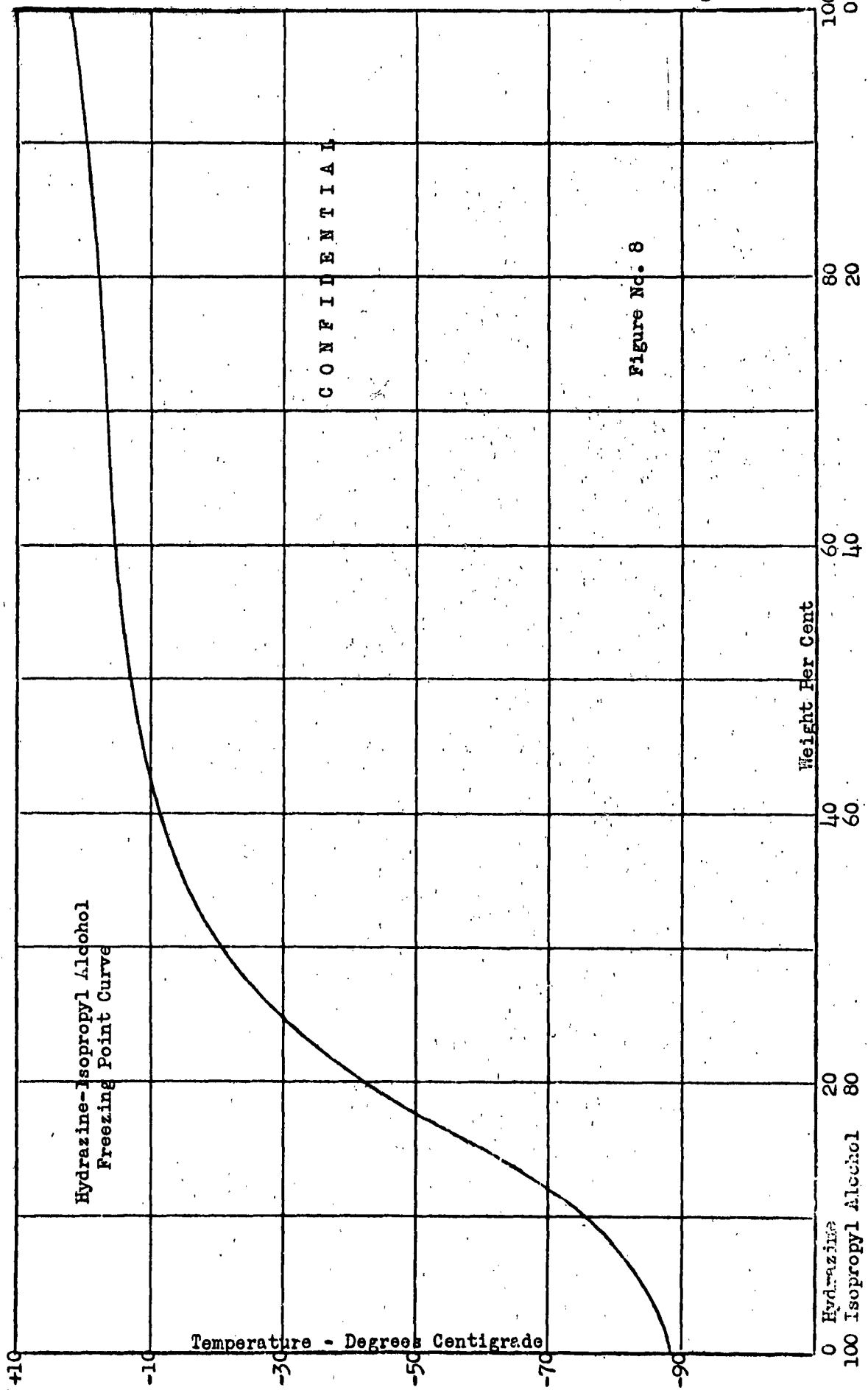and Hydrazine with Liquid Oxygen

A.   Hydrazine
B.   Methylhydrazine
C.   Uns-Dimethylhydrazine

Figure No. 11

Mixture Ratio - O/F
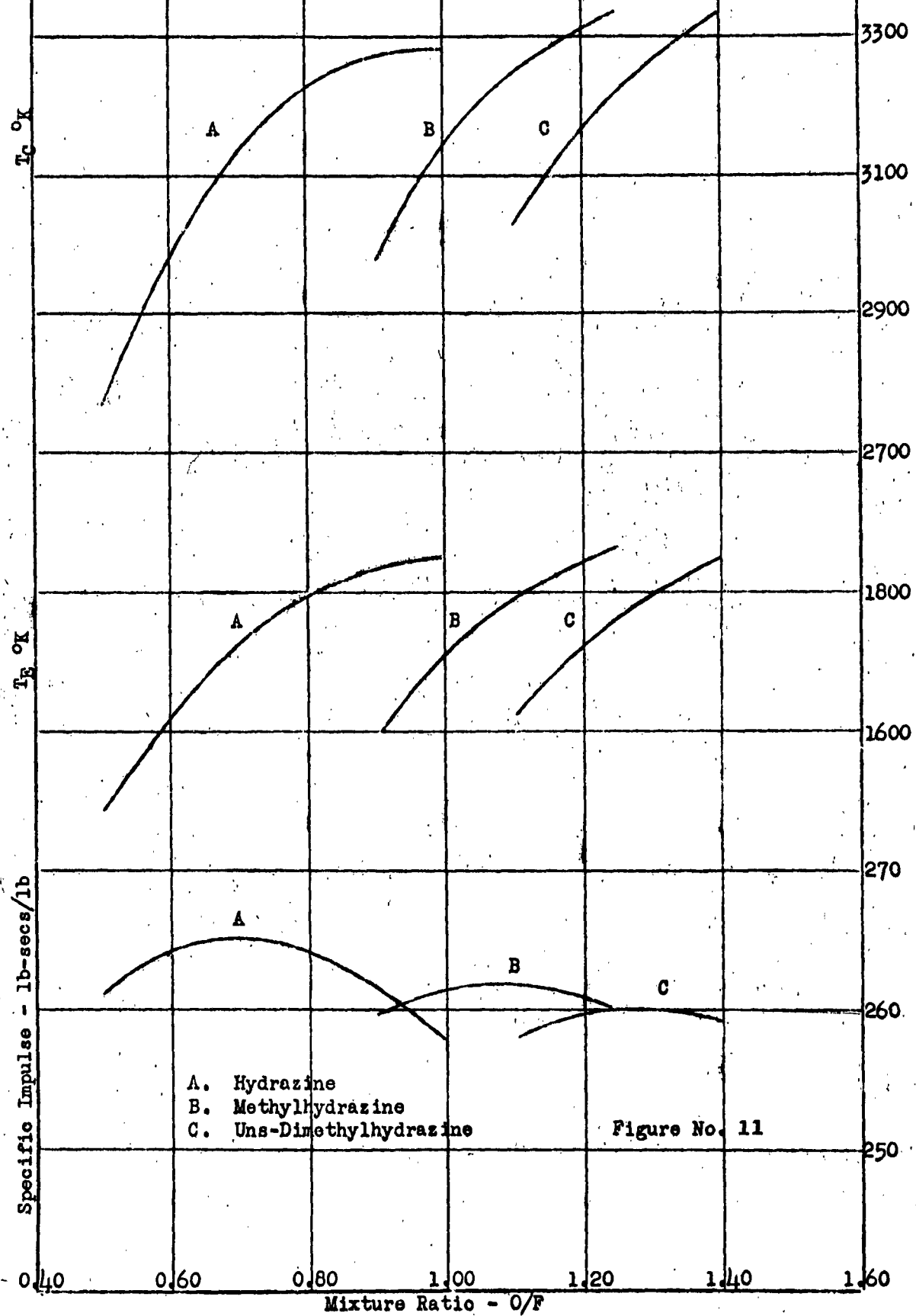
FIGURE NO. 12

CATALYTIC INFLUENCE IN THE OXIDATION OF
ANHYDROUS HYDRAZINE AND METHYLATED HYDRAZINES

Hydrazine

Methylhydrazine

UDMH

Sym-Dimethylhydrazine

Trimethylhydrazine

Tetramethylhydrazine
Minutes
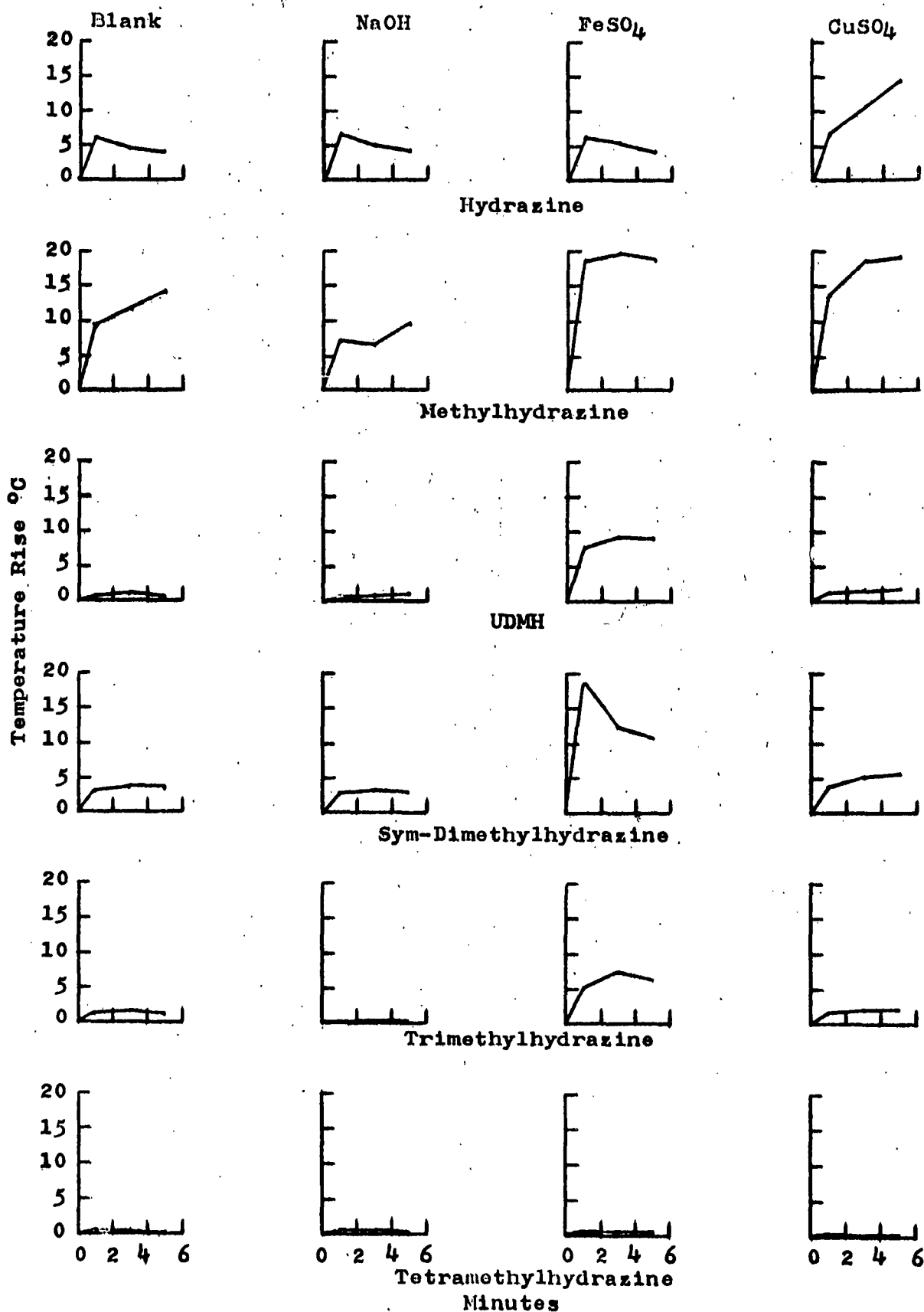
FIGURE NO. 13

CATALYTIC INFLUENCE IN THE OXIDATION OF
AQUEOUS SOLUTIONS OF METHYLATED HYDRAZINES

Blank   NaOH   FeSO$_4$ CuSO$_4$

Hydrazine

Hydrazine

Methylhydrazine

Methylhydrazine

Hours
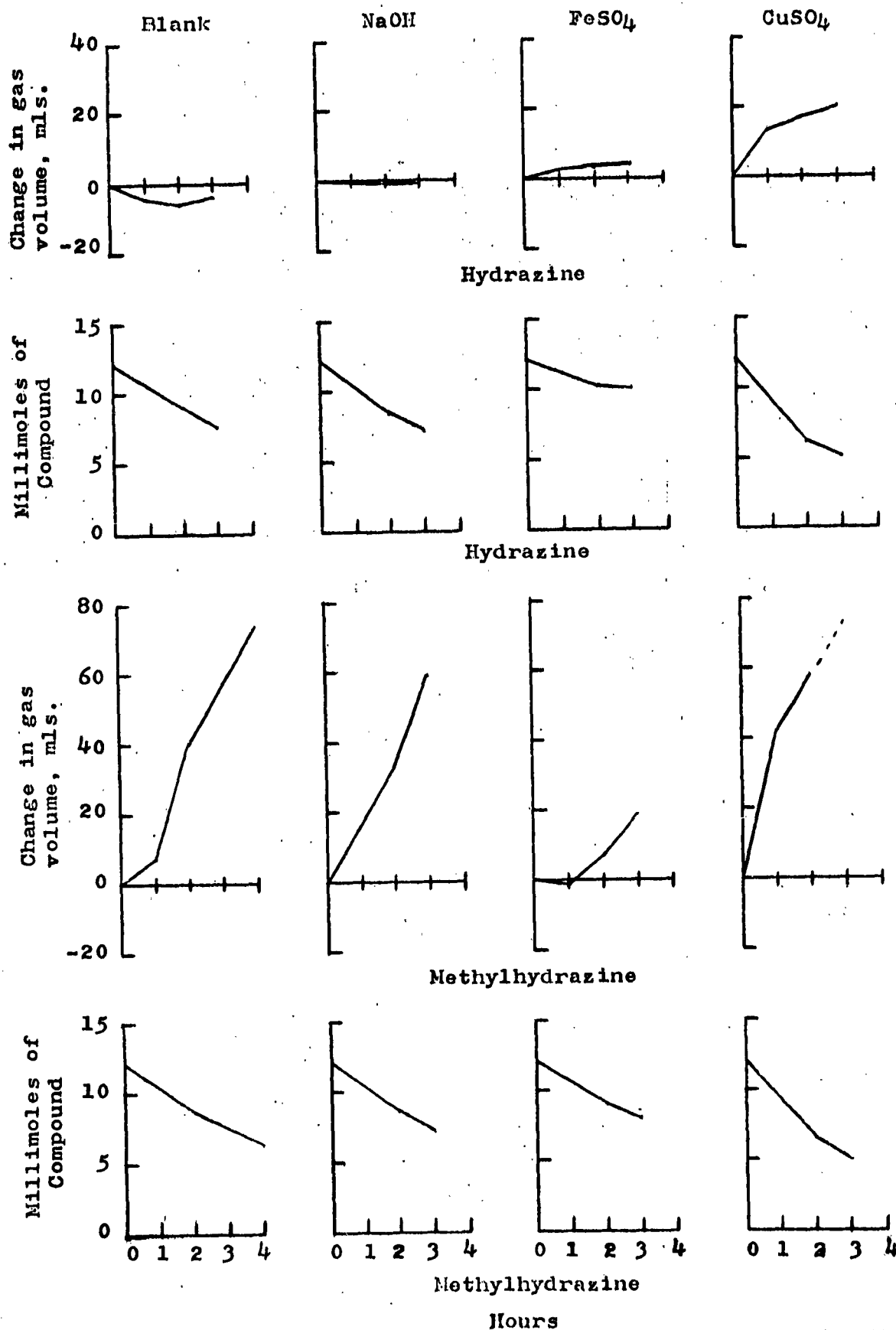
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FIGURE NO. 14

CATALYTIC INFLUENCE IN THE OXIDATION OF
AQUEOUS SOLUTIONS OF METHYLATED HYDRAZINES

Sym-Dimethylhydrazine

Hours
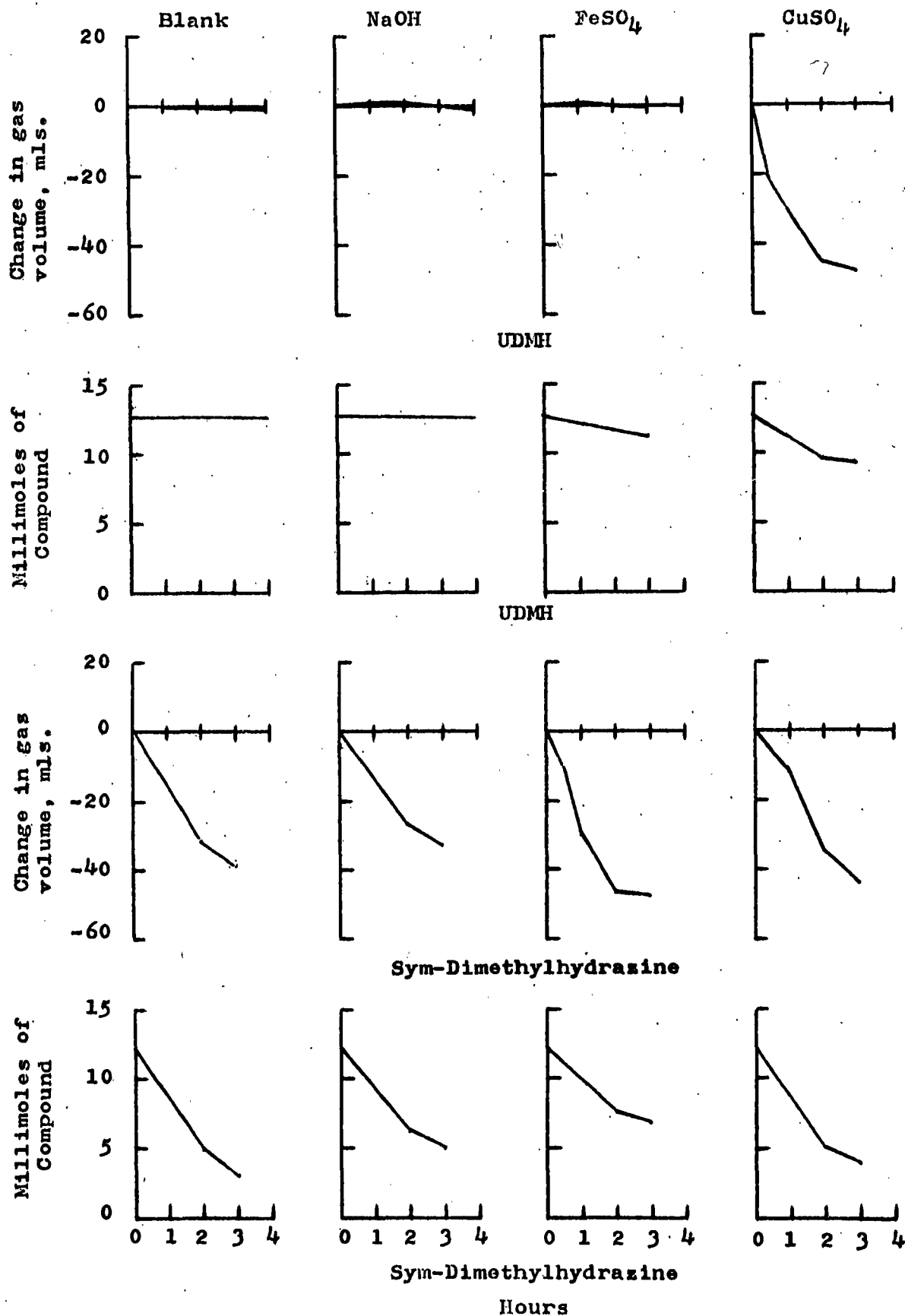
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FIGURE NO. 15

CATALYTIC INFLUENCE IN THE OXIDATION OF
AQUEOUS SOLUTIONS OF METHYLATED HYDRAZINES

Trimethylhydrazine

Trimethylhydrazine

Tetramethylhydrazine

Tetramethylhydrazine

Hours

Methylhydrazine–Hydrazine
Freezing Point Curve

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Figure No. 16

Temperature – Degrees Centigrade

Weight Per Cent

0 Hydrazine
100 Methylhydrazine

Uns-Dimethylhydrazine-Hydrazine
Freezing Point Curve

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Figure No. 17

Weight Per Cent

Hydrazine
100 Uns-Dimethylhydrazine

Temperature - Degrees Centigrade

Page 97

Methylhydrazine-Water
Freezing Point Curve

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Figure No. 18

Temperature - Degrees Centigrade

+10   -10   -30   -50   -70   -90

Weight Per Cent

0   20   40   60   80   100
0 Water
100 Methylhydrazine   80   60   40   20   0

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Uns-Dimethylhydrazine-Water
Freezing Point Curve

Temperature-Degrees Centigrade

Weight Per Cent

Water
100 Uns-Dimethylhydrazine

Figure No. 19

Uns-Dimethylhydrazine-Methylhydrazine
Freezing Point Curve

Figure No. 20

Temperature - Degrees Centigrade

Weight Per Cent

FIGURE NO. 21

TITRATION CURVE OF METHYLHYDRAZINE

Weight of Sample: 0.1095 gms
Normality of HCl: 0.09567

FIGURE NO. 22

TITRATION CURVE OF UNS-DIMETHYLHYDRAZINE

Weight of Sample: 0.1524 gms
Normality of HCl: 0.09567

pH

Volume, mls.

FIGURE NO. 23

TITRATION CURVE OF SYM-DIMETHYLHYDRAZINE

Weight of Sample: 0.1791 gms
Normality of HCl: 0.09567

Volume, mls.

pH

FIGURE NO. 24

TITRATION CURVE OF TRIMETHYLHYDRAZINE

Weight of Sample: 0.1778 gms
Normality of HCl: 0.09567

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FIGURE NO. 25

TITRATION CURVE OF TETRAMETHYLHYDRAZINE

Weight of Sample: 0.1519 gms
Normality of HCl: 0.09567

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